HYDROGEOCHEMISTRY OF A BURIED PREGLACIAL CHANNEL
IN SOUTHEAST MARSHALL COUNTY, KANSAS

by

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A MASTER'S THESIS

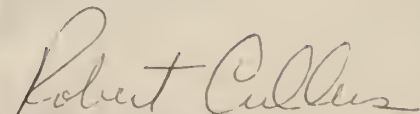submitted in partial fulfillment of the

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PURPOSE OF INVESTIGATION

Buried bedrock channels in the glaciated region of northeast Kansas have been recognized for many years as potential sources of good quality ground water. Ground-water yields of up to several hundred gallons per minute (gpm) are possible from the buried channel aquifers, representing some of the largest yields in the region. Several rural water districts and municipalities in northeast Kansas are developing the water resources of these buried channels because of this potential for large ground-water yields. This investigation examined the hydrogeology and hydrogeochemistry of part of the buried channel in Marshall County. The purpose of the investigation was to: 1) further define the orientation and cross-sectional profile of the channel; 2) determine the distribution of chert gravels frequently found along the axis of the channel; 3) evaluate the water quality of hydrogeologic units in the region; 4) determine the sources and controls for the dissolved constituents in the ground water; and 5) evaluate possible sources of ground-water recharge to the buried channel.

The buried channel in southeast Marshall County supplies water to Rural Water District 3 (RWD3), Marshall County, and Frankfort (Fig. 1). RWD3 pumped about 50 million gallons of water annually from the buried channel in 1983 and 1984. The maximum pumping rates from these wells are estimated at up to 300 gpm (Schwab-Eaton, 1976) and are clearly the largest capacity wells in the area. A few smaller domestic wells in southeast Marshall County also produce water from the buried channel.
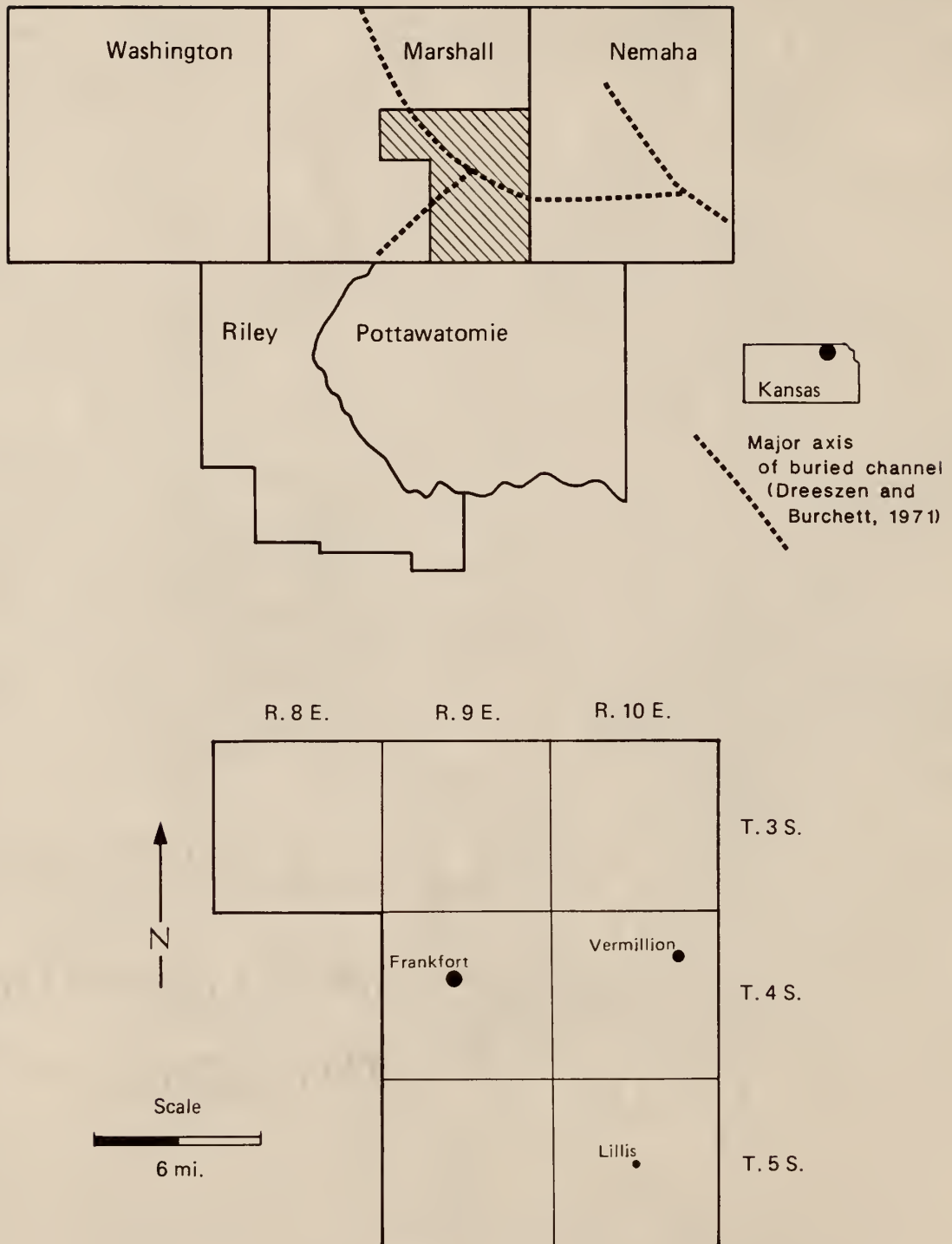
Figure 1 -   **Index map of southeast Marshall County, northeast Kansas**

A literature search was conducted for well logs and hydrochemical data for wells in the investigation area. The orientation and cross-sectional profile of the buried channel were further defined by geologic reconnaissance and test hole drilling. The major-ion concentrations of ground-water samples collected from the various aquifers in the area were measured to determine the sources and controls for the dissolved constituents in the ground water. Based on the hydrogeologic and hydrochemical data collected, possible sources of ground-water recharge to the channel were evaluated.

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To my wife Sandra, and to Lucas, Timothy, and Allison, my sincerest appreciation for their continued moral support, patience, and encouragement during my undergraduate and graduate studies.

AREA OF INVESTIGATION

The investigation area is in southeast Marshall County, Kansas, and includes seven townships, encompassing 250 square miles (Fig. 2). This area lies within the Dissected Till Plains section of the Central Physiographic Province of the Interior Plains region (Schoewe, 1949, p. 272). The ground surface in most areas is characterized by gently undulating till-mantled hills of low topographic relief, locally seldom exceeding 100 feet. Topographic relief can approach several hundred feet in areas underlain by surface exposures of marine limestones and shale bedrock.

Black Vermillion River and its tributaries are the principal surface water drainages. Flow in streams is southwestward across till-mantled areas, which generally occurs throughout the year. Robidoux Creek is the principal tributary drainage from the north and joins Black Vermillion River one mile southwest of Frankfort. Irish and Clear Fork creeks are smaller northward-flowing streams. These creeks flow across bedrock in the southern one-third of the area.

Marshall County has a continental climate characterized by large daily and annual variations in temperature. Average daily temperatures are 28°F in winter and 76°F in summer; annual rainfall is about 31 inches, 76 percent of which usually falls between April and September, and snowfall averages about 20 inches per year (SCS, 1980). Potential lake evaporation is about 46 inches per year (Kohler et al., 1959), which is greater than average annual rainfall.
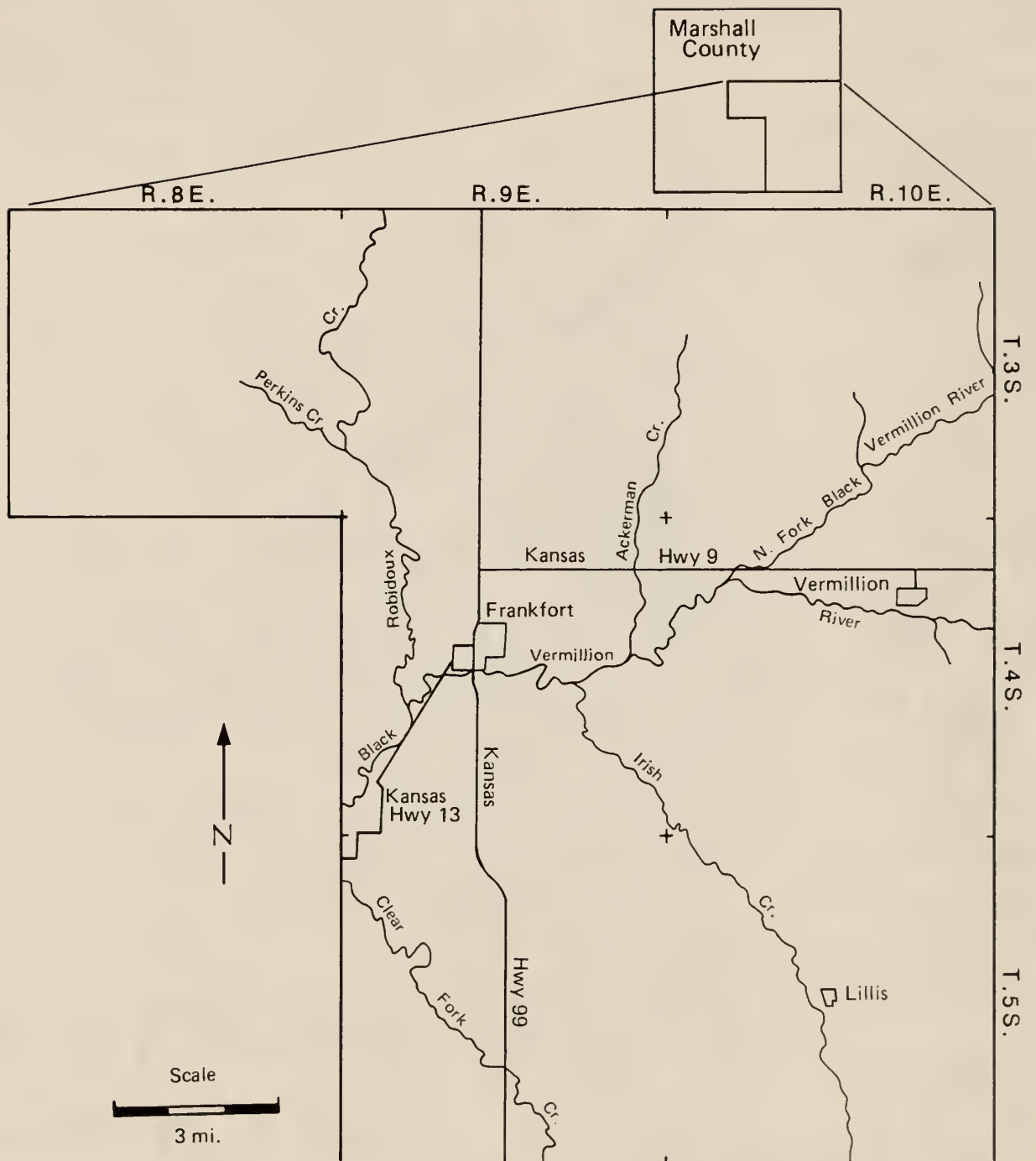
Figure 2 - **Map of investigation area in southeast Marshall County**

The predominant industry in the area is agriculture. The predominant crops include corn, wheat, alfalfa, oats, and soybeans. Alluvium along streams such as Black Vermillion River and Robidoux Creek is commonly under cultivation. Upland areas underlain by bedrock are generally uncultivated, native grassland.

PREVIOUS INVESTIGATIONS

Previous hydrogeologic investigations of Marshall County are few in number, although several early regional investigations described the geology of Marshall County. The focus of many early studies was the stratigraphy of bedrock and glacial deposits in the state. Notable among these early regional studies are Moore et al. (1940), Frye and Leonard (1949, 1951, 1952), Moore et al. (1951), Reed et al. (1965), and Zeller (1968). The massive gypsum deposits (up to 8 feet thick) in eastern-central Marshall County were described by Fairchild (1947), Kulstad et al. (1956), and Pflug (1963a, 1963b). Frye and Walters (1950) described the subsurface stratigraphy of glacial deposits in northeast Kansas and generally were first to delineate the buried bedrock channel in southeast Marshall County (Frye and Walters, 1950, plate 1).

The only comprehensive hydrogeologic investigation of Marshall County was conducted by Walters (1954). The geology and ground-water resources of the county, including ground-water quality, were described. Geologic logs of 60 test borings and wells indicate the buried channel in Marshall County is a broad, subtle depression in the bedrock surface. Axis of the channel crosses under the present courses of Robidoux Creek and the Black Vermillion River a few miles north of Frankfort (Walters, 1954, p. 58 and plate 2) (Fig. 1).

Maximum topographic relief of bedrock beneath glacial deposits is about 200 feet over a horizontal distance of 6 miles.

Historical water-quality data (Walters, 1954, Table 3, Figs. 6 and 7) indicate ground water in the region is moderately mineralized and predominantly Ca-HCO$_3$-type water; however, other water types exist, especially in bedrock aquifers where highly mineralized Ca-SO$_4$-type water is common. These data also show that ground water in the buried channel in Marshall County appears to be generally of good quality indicating that ground-water recharge to the buried channel from subsurface flow out of the bedrock is minimal or that ground water in the bedrock is not highly mineralized in some areas.

The geographic distribution of chemically distinct water types generally coincides with aquifer rock type (Walters, 1954, p. 63 and plate 3), which suggests the sources and controls for dissolved constituents in the ground water are, in part, a function of aquifer rock type (Bricker and Garrels, 1967).

Ward (1974) described the geology and ground-water resource of Nemaha County. The configuration of the bedrock surface beneath glacial drift (Ward, 1974, p. 8, Fig. 3) shows the well-developed preglacial drainage. Flow was southeastward into the Grand River drainage (Heim and Howe, 1963), which flowed across much of the mid-continent region. The buried channel in Marshall County was probably once part of the ancestral Grand River drainage (Dreeszen and Burchett, 1971, Fig. 1).

Ground-water quality in Nemaha County is similar to that in Marshall County, although some major differences exist. High concentrations of some ions in ground water from the buried channel in Nemaha County, especially

concentrations of sulfate, suggest that in some areas a significant component of ground-water recharge to the buried channel is underflow from underlying bedrock (Ward, 1974, p. 19 and Figs. 3, 4, 8, and 9). This subsurface flow has severely degraded the ground-water quality in some parts of the buried channel in Nemaha County, in some cases making the water nonpotable.

RELATION OF GEOLOGY TO GROUND WATER

GENERAL GEOLOGY

Bedrock in the investigation area consists of Upper Pennsylvanian and Lower Permian marine limestone and shale. The bedrock is unconformably overlain in some areas by Pleistocene glacial deposits and Recent alluvium. Figure 3 shows the stratigraphic sequence in the investigation area.

Bedrock exposures in southeast Marshall County consist mainly of Lower Permian strata (Fig. 4). Outcrops of Pennsylvanian strata are restricted to a few widely scattered exposures in the extreme eastern part of the region. A maximum of about 500 feet of bedrock is exposed. The regional dip of bedrock is westward at roughly one-sixth degree or 15 feet per mile.

Pleistocene deposits overlying bedrock are unconsolidated and generally were deposited as a result of continental glaciation during the Kansan Glacial Stage (Walters, 1954, p. 58). The oldest Pleistocene deposits are Pre-Kansan chert gravels that are generally considered of preglacial age (Frye and Walters, 1950, p. 147; Ward, 1974, p. 9). The lack of igneous and metamorphic rock fragments in the chert gravels, a common component of younger glacial deposits, indicates they were probably locally derived from erosion of chert-bearing limestone bedrock.

The chert gravels were deposited directly on the bedrock surface by east-flowing streams and appear to be restricted to the axis of the buried channel (Ward, 1974, p. 9). The gravels are overlain by younger Pleistocene glacial deposits and are not exposed anywhere in the region. Maximum thickness of the chert gravels is about 22 feet based on driller's logs.

Sys.	Ser.	Stg.	Gp.	Formation	Member	Thickness, ft.
Quaternary	Pleistocene	Recent		Alluvium		0-50
		Wis.		Sanborn	Peoria Silt / Loveland Silt	0-20
				Meade	Sappa / Grand Island	0-55
		Ill.		Kansan Till		0-325
		Kansan		Atchison		0-115
		Nebraskan		Pre-Kansan Gravels		0-22
Permian	Lower Permian	Gearyan	Chase	Doyle Shale	Gage Shale / Towanda Limestone / Holmesville Shale	70-80
				Barneston Limestone	Fort Riley Limestone / Oketo Shale / Florence Limestone	45-65
				Matfield Shale	Blue Springs Shale / Kinney Limestone / Wymore Shale	55-65
				Wreford Limestone	Schroyer Limestone / Havensville Shale / Three Mile Limestone	30-40
			Council Grove	Speiser Shale		15-20
				Funston Limestone		5-7
				Blue Rapids Shale		14-20
				Crouse Limestone		6-8
				Easly Creek Shale		15-20
				Bader Limestone	Middleburg Ls / Hooser Shale / Eiss Limestone	17-22
				Stearns Shale		17-20
				Beattie Limestone	Morrill Limestone / Florena Shale / Cottonwood Ls	11-19
				Eskridge Shale		24-28
				Grenola Limestone	Neva Limestone / Salem Point Shale / Burr Limestone / Sallyards Limestone	35-40
				Roca Shale		20-28
				Red Eagle Limestone	Howe Limestone / Bennett Shale / Glenrock Limestone	9-16
				Johnson Shale		15-20
Pennsylvanian	Upper Pennsylvanian		Admire	Foraker Limestone	Long Creek Ls / Hughes Creek Shale / Americus Limestone	40-50
				Janesville Shale	Hamlin Shale / Five Point Limestone / West Branch Shale	125-150
			Wabaunsee	Falls City Limestone		
				Onaga Shale	Hawxby Shale / Aspinwall Limestone / Towle Shale	
				Woodsiding	Brownville Ls / Pony Creek Shale	14

Figure 3 - **Stratigraphic section (after Zeller, 1968)**
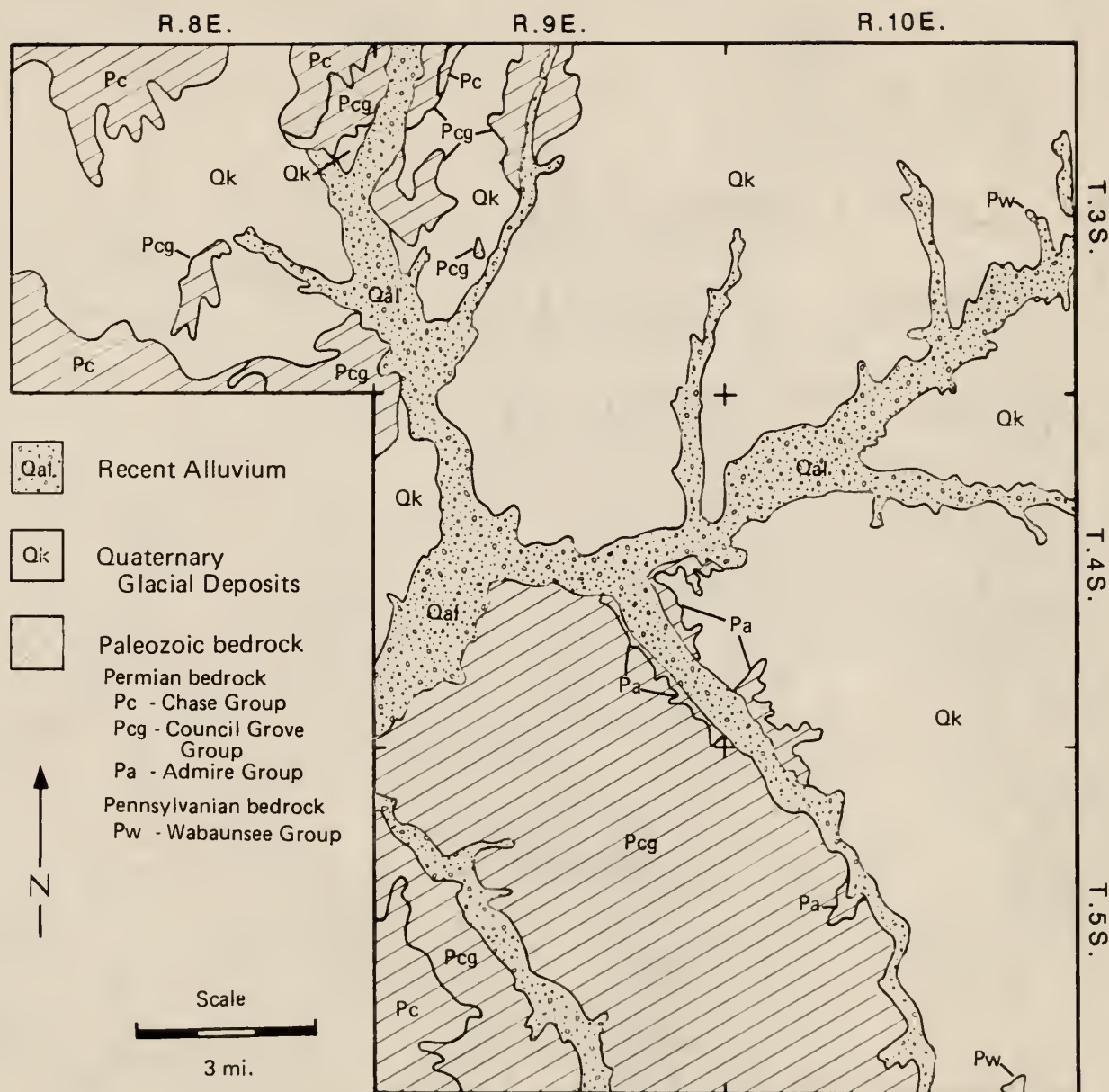
Figure 4 - **Generalized geologic map of southeast Marshall County (modified from Walters, 1954)**

Proglacial deposits and till comprise the greatest volume of the Pleistocene deposits. The proglacial deposits consist of clays, silts, sands, and gravels and overlie bedrock or chert gravels. They are not exposed in the investigation area. Sediments were derived from meltwaters of the advancing Kansan ice sheet and were deposited in proglacial streams and lakes (Frye and Leonard, 1952, p. 71). The proglacial gravels contain a large percentage of igneous and metamorphic rock fragments and are easily distinguished from preglacial chert gravels. Maximum thickness of the proglacial deposits is about 120 feet based on boring logs.

Kansan till or drift is the predominant Pleistocene deposit. The till generally overlies proglacial deposits or bedrock and consists of a silty clay matrix containing boulders of various lithologies, especially pink quartzite. In some areas, the till may overlie preglacial chert gravels. The till is only slightly younger than the proglacial deposits as evidenced by the lack of a prominant intervening soil horizon (Frye and Leonard, 1952, p. 71). The glacial deposits, including chert gravels, proglacial deposits, and till, attain a maximum thickness of about 335 feet along the axis of the buried valley near the Marshall-Nemaha county line (Walters, 1954, p. 97).

Late Pleistocene ice sheets did not reach Kansas. The earlier glacial sediments were subjected to erosion and weathering following retreat of the Kansan ice sheet (Frye and Walters, 1950, p. 152). Deposition of extensive loess sheets and development of soils at several horizons occurred during the Late Pleistocene.

BEDROCK STRATIGRAPHY AND MINERALOGY

Pennsylvanian System

Rocks of the Wabaunsee Group occur at the surface or at depth beneath glacial deposits in eastern Marshall County. About 50 feet of Pennsylvanian age rocks are exposed, including the upper part of Pony Creek Shale and overlying Brownville Limestone. Rocks older than the Wabaunsee Group do not crop out in the area. In eastern Marshall County, rocks of the Wabaunsee Group form the walls of the buried channel where it is deeply incised into the bedrock and covered by several hundred feet of till.

The Pony Creek Shale is a silty to sandy, highly calcareous shale (Ward, 1974). The clay fraction is composed of predominantly illite (Watkins, 1957). The Brownville Limestone consists of highly fossiliferous limestone beds. Wells in Marshall County are not known to yield water from Pennsylvanian bedrock (Walters, 1954). Sandstone aquifers of the Wabaunsee Group may occur at great depths and could yield water if penetrated by wells. These sandstones could also supply water to the buried channel by underflow where they have been deeply eroded.

Permian System

Permian rocks form about 40 percent of surface exposures in the region and comprise the bedrock surface that underlies much of the Pleistocene deposits (Fig. 4). Rocks of the Admire, Council Grove, and Chase groups are exposed in southeast Marshall County. The Council Grove is the only Permian group exposed in its entirety in the investigation area.

The Admire Group is the oldest group of the Permian System and consists chiefly of about 130 feet of shale beds and some thin, intervening limestone

and sandstone beds (Walters, 1954, p. 40). Shale members are variegated, clayey to sandy, and calcareous. Illite is the predominant clay mineral of the shales (Asmussen, 1958). Some limestone formations also contain illite (Twiss, 1955).

The upper 16 feet of the Admire Group crops out southeast of Frankfort along the south valley wall of the Black Vermillion River and along Irish Creek. Wells in Marshall County are not known to produce water from shale beds because of their limited permeability. The intervening limestone beds are generally too thin to produce water and are isolated from recharge by shale beds above and below.

The Council Grove Group overlies the Admire Group and underlies the Chase Group. The group consists of 14 formations of limestone and shale strata, which crop out south of Frankfort and along Robidoux Creek. The total thickness is over 240 feet of mainly limestone strata. Limestone beds range from 1 to 7 feet thick and generally are thicker than those of the Admire Group (Zeller, 1968, p. 44-45). They are soft to hard and massive, and contain a variety of fossils. Shale beds are similar to those of the Admire Group, but are generally thinner.

The predominant clay mineral of the shale beds is illite (Dulekoz, 1966; Asmussen, 1958; Dowling, 1967). Gypsum in the limestone units was not observed in outcrop, but is abundant in the subsurface (Walters, 1954; Amoco, 1975; Whittemore et al., 1982). Dolomite and celestite have been reported as secondary minerals in some formations (Watkins, 1957; Hargadine, 1959). Some limestone beds, including the Neva Limestone and Cottonwood Limestone, are cavernous or jointed and fractured and form conspicuous outcrops, especially south of Frankfort.

Limestone beds of the Council Grove Group, including selected members of the Grenola Limestone, Beattie Limestone, and Bader Limestone, form major bedrock aquifers in many parts of Marshall County (Walters, 1954). Jointing and dissolution have produced high secondary porosity and permeability, resulting in greatly increased ground-water yields. A single limestone bed in each of these formations is commonly responsible for the observed ground-water yield.

The Grenola Limestone generally has the greatest ground-water yield of any bedrock aquifer. The formation occurs at the surface south of Frankfort and in the shallow subsurface northwest of Frankfort. The Neva Limestone Member is probably the principal water-bearing strata of the Grenola Limestone. Many perennial springs issue from limestone beds of the Neva Limestone.

The Bader Limestone and Beattie Limestone form major aquifers in the western part of Marshall County. However, these formations are not major aquifers in the investigation area because they generally occur above the water table or are partially or completely eroded. The Cottonwood Limestone Member of the Beattie Limestone may form an important aquifer in the extreme southwestern and northwestern parts of the investigation area.

The Chase Group overlies the Council Grove Group and consists of alternating limestone and shale strata. Outcrops are limited to the extreme northwestern part of the area where the lower 150 feet of the group are exposed. The lower part of the Doyle Shale Member is the youngest exposed bedrock.

Limestone beds are massive and commonly contain chert as bands or scattered nodules. Gypsum is present in limestone beds in the subsurface (Amoco, 1975). Many limestone beds are highly fractured in outcrop. Shale

beds are similar to other underlying Permian shale strata. Formations of this group are generally above the water table, but locally may yield small quantities of ground water.

QUATERNARY STRATIGRAPHY AND MINERALOGY

Pleistocene Series

Basal Chert Gravels.--Pre-Kansan chert gravels are the oldest Pleistocene deposits and are mainly found at the base of the buried channel. The gravels are generally very coarse and attain a maximum grain size of about 1 inch in diameter (Beck, pers. comm.). Limestone fragments also occur in the gravels, although they are far less abundant than the chert. Ground-water yields of up to several hundred gpm are possible from the chert gravels. These deposits constitute an important aquifer, regardless of their limited distribution along the buried channel's axis.

Glacial Deposits.--The Atchison Formation is the oldest of the Kansan glacial deposits (Reed et al., 1965, p. 195). It is generally confined to the buried valley where it overlies basal chert gravels or bedrock and underlies Kansan Till (Ward, 1974, p. 9). The formation is an unconsolidated proglacial sand, which is comprised of very fine sand and silt consisting of mainly quartz. Thickness of the Atchison Formation is highly variable. The maximum thickness is probably 100 feet or slightly more based on well log data. Ground-water yields are generally small to moderate (Walters, 1954, p. 59).

Kansan Till overlies the Atchison Formation or bedrock and forms the ground surface in much of southeast Marshall County. Like most of the Pleistocene deposits, the till is unconsolidated. The till consists of a fractured clay to silty clay matrix containing abundant rock fragments

covering an extremely wide range of grain sizes. Glacial erratics consisting
of blocks of quartzite are common in the till and range in size up to tens of
feet in diameter. Deposits of silt, sand, and gravel are randomly
interstratified in the till and probably originated from intratill streams.

The till generally yields only small quantities of ground water because it
has low primary permeability; however, fractures in the till matrix increase
the bulk permeability by 10 to 100 times (Grisak and Cherry, 1975, p. 42).
The highest ground-water yields in the till come from intratill gravel lenses,
but sustained ground-water yields are doubtful because these gravels are
generally isolated from recharge by the clayey till.

The till consists of a diverse assemblage of minerals. The most common
minerals are smectites, feldspars, quartz, calcite, dolomite, and minor gypsum
(Grisak et al., 1976, p. 320). The smectites are probably the most
volumetrically abundant mineral group; however, calcite and dolomite are
ubiquitous in the till. The calcite and dolomite occur as rock fragments of
eroded bedrock and as secondary mineralization along fracture planes (Grisak
et al., 1976 and Hendry et al., 1986). Gypsum also occurs as a secondary
mineral in fractures.

Holocene Series

River valleys of present day streams are underlain by alluvium consisting
of clay, silt, sand, and gravel. Thickness of the alluvium is uncertain in
many areas, but is probably up to about 50 feet thick based on well logs. The
alluvium is generally saturated throughout and its association with
permanently flowing streams makes the alluvium favorable for ground-water
development; however, few wells in the alluvium are known to exist in
southeast Marshall County.

METHODS OF INVESTIGATION

Field Methods

Field methods used in this investigation included geologic reconnaissance, test hole drilling, and ground-water sampling. Geologic reconnaissance was conducted to locate bedrock outcrops within the glacial drift as an aid to locating the axis of the buried channel. Selected areas were examined in the field following review of the existing geologic map by Walters (1954) and the Soil Conservation Service (SCS) map for the county (SCS, 1980). Most of the geologic reconnaissance was conducted along county roads. Creek channels were examined for outcrops and eroded fragments of bedrock.

Subsurface geologic information was obtained by test hole drilling through glacial drift to the bedrock surface at locations determined by Beck (pers. comm.). Test holes were installed at eight locations using a Failing rotary drill rig and truck-mounted four-inch-diameter continuous-flight hydraulic auger. The drilling equipment was provided by the Kansas Geological Survey. Drill cuttings were logged according to standard geologic classifications.

Ground-water samples were collected from 42 existing private wells constructed in bedrock, glacial deposits, or buried channel gravels (Fig. 5). Sixty-two samples were collected from the wells between July 1982 and September 1983, with up to four samples collected from a few wells. The 62 samples collected include 10 from buried-channel gravels, 34 from glacial deposits, and 18 from bedrock. Samples were not collected from alluvial deposits because no wells could be located. Wells were chosen for sampling based on their geographic location relative to the buried channel, aquifer penetrated, approximate depth, plumbing configuration, and ease of access.

Figure 5 - **Locations of wells from which ground-water samples were collected**

Wells and test borings were located according to the Bureau of Land Management System of land subdivision. Accordingly, the number of a well describes its location. This numbering system consists of, in the following order: township, range, and section number followed by up to three lower case letters designating the quarter section, quarter-quarter section, and quarter-quarter-quarter section (10-acre tract). The letters are assigned in a counterclockwise direction, beginning with the letter 'a' in the northeast corner of each quarter section, quarter-quarter section, and 10-acre tract, respectively. Two or more wells in the same 10-acre tract are numbered serially according to order inventoried. Serialization is not used when only a single well was located in a 10-acre tract.

Ground-water sampling and preservation techniques are those of Skougstad et al. (1979) and are summarized on Table 1. Wells were pumped for about 20 minutes prior to sampling to remove stagnant water from the well bore and permit the flow of fresh ground water into the well. Ground-water pH, specific electrical conductivity (SEC), and temperature were monitored during well purging to indicate when water representative of the formation was obtained.

Samples were collected at each location following three subsequent pH readings within 0.1 pH unit. Two liters of ground water were collected and filtered in the field using a 0.45 micrometer membrane filter. Sampling equipment was rinsed several times with a filtered portion of sample water prior to final sample collection.

One liter of sample was acidified to pH 2-3 using approximately 2-4 mL of 8 N nitric acid. The metals determinations were performed on this acidified sample. A second liter of ground water was collected, but was not acidified.

Table 1. Preservation Techniques for Ground-Water Samples

Constituent or Parameter	Technique
Ca, Mg, Sr, Na, K	Pressure filter immediately with 0.45 micrometer membrane filter and acidify to pH 2-3 with 2 mL 8N HNO_3. Store on ice for transport to laboratory.
HCO_3, Cl, SO_4, NO_3	Pressure filter immediately with 0.45 micrometer membrane filter. Store on ice for transport to laboratory.
pH, Temperature, Specific Electrical Conductance	Measure at time of sample collection.

This unacidified sample was used for analysis of the anions. Air bubbles were carefully removed before sealing sample bottles to minimize loss of dissolved gases. Samples were stored in ice chests for transport to the laboratory.

Laboratory Methods

Major-ion chemical analyses were performed on ground-water samples. Analytical techniques used in the chemical analysis of ground-water samples and approximate analytical uncertainty for each method are shown on Table 2. Specific laboratory and field techniques and procedures used in the chemical analyses are shown in Appendix A. A brief description of each analytical method is provided below.

Metals concentrations were determined by atomic absorption and emission spectrophotometry on a Perkin-Elmer 305B atomic absorption spectrophotometer. The metals determinations were performed within one to two weeks of sample collection. Bicarbonate concentrations were determined by titration with standardized H_2SO_4 to an end point of pH 4.5. The bicarbonate measurements were made on a chilled, unacidified sample within 24 hours of sample collection. Sulfate was determined by turbidimetry using a Coleman spectrophotometer and barium chloride as a precipitating agent for the sulfate. Chloride content was measured by Mohr titration to the silver chromate end point. Nitrate determinations were done by UV-spectrophotometry. Determinations of sulfate, chloride, and nitrate concentrations were conducted generally within one to two weeks of sample collection. All samples were stored in a refrigerator at a temperature of about 5°C until the analyses were completed and verified by calculating the cation-anion charge balance.

Table 2. Analytical Methods Used in Analysis of Ground-Water Samples
and Approximate Percent Precision

Constituent or Property	Method*	Precision, percent
Ca, Mg, Sr	Atomic absorption spectrophotometry	3
Na, K	Flame emission spectrophotometry	3
HCO_3, Cl	Titrimetry	3
SO_4	Turbidimetry	6
NO_3	UV-Spectrophotometry	5
pH	Potentiometry	1
Temperature	Thermometry (mercury)	1
Specific Electrical Conductance	Conductimetry	2

* Appendix A contains detailed descriptions and references for each analytical
method.

The computer code WATEQF (Plummer et al., 1976) was used to calculate geochemical parameters of interest, including cation-anion charge balance, carbon dioxide partial pressure, ion speciation, and saturation indices.

R E S U L T S   A N D   D I S C U S S I O N

HYDROGEOLOGY

Four hydrogeologic units or aquifer types are identified based on gross physical and chemical hydrogeologic characteristics of the geologic deposits. The four units identified are bedrock, glacial deposits, buried channel gravels, and alluvium. These designations are similar to those of Walters (1954, plate 3) and Whittemore et al. (1982) although the divisions used here are slightly different.

Bedrock

Bedrock aquifers generally consist of limestone beds, which have high secondary porosity and permeability from post-depositional fractures and solution channels. These features have a major impact on ground-water movement; however, wells in bedrock aquifers are capable of maximum yields of no more than about 10 gpm (Beck, 1983, pers. comm.). These wells are generally used for domestic or stock water supplies. Because well construction details were sometimes not available or indicated a gravel pack across several limestone units, it was not possible to identify the particular limestone unit that supplied water to a well. Based on topography and estimated depths of many wells, it appears that members of the Grenola Limestone or Beattie Limestone comprise the aquifer units in many bedrock areas.

Regional ground-water flow directions were not determined in this investigation because ground-water movement is locally controlled by many factors, including soil type, topography, stratigraphy, and fracture patterns, and water levels measured in wells are affected by varying well construction

techniques. Also, the density of wells in the investigation area was inadequate to permit such a determination.

Water levels in bedrock aquifers were estimated in a few wells from driller's logs. The depth to water is commonly 35 to 80 feet below ground surface. The water table surface in fractured bedrock is probably irregular and ground water is probably unconfined (Fetter, 1980, p. 224; Lattman and Parizek, 1964, p. 87). A relationship between water levels and recharge and discharge could not be established with the limited data available.

Ground-water recharge occurs by infiltration of precipitation, which falls directly on outcrop areas. Regional underflow from adjacent areas and percolation through overlying unconsolidated deposits such as glacial deposits or alluvium, probably also contributes to recharge. The rate of ground-water recharge is relatively rapid for some bedrock aquifers. Whittemore et al. (1982) showed that a large proportion of the recharge to Permian limestones occurred within a period of a few months following the onset of wet spells, suggesting much of the recharge originates locally as rainfall.

Ground-water discharge occurs as evapotranspiration, flow from springs, and regional underflow. Flow commonly occurs from bedrock aquifers to overlying glacial deposits or alluvium (Whittemore et al., 1982, p. 30). Several springs issue from solution zones in the Neva Limestone along cliffs on Clear Creek. These springs indicate the underlying shale beds are generally impermeable, inhibiting direct vertical migration of ground water. Ground water in permeable limestone aquifers generally moves in the direction of dip when it encounters impermeable shale beds (Walters, 1954, p. 20).

Buried Channel

The shape of the bedrock surface beneath glacial deposits was determined from well logs and the locations of bedrock outcrops as shown in Figure 6. The depth to bedrock in wells is shown in Table 3. The geologic logs of test borings installed for this investigation are contained in Appendix B.

The axis of the channel trends from northwest to southeast across the investigation area (Fig. 7). Cross sections of the channel (Figs. 8 and 9) show it is asymmetrical and broad near the Marshall-Nemaha County line and narrow in the northwestern part of the region. The channel appears to pass under the alluvium of Robidoux Creek and the Black Vermillion River a few miles north of Frankfort.

The gradient of the bedrock surface along the channel's main axis is to the southeast at about 4 to 5 feet per mile. The bedrock surface below the alluvium of the Black Vermillion River southwest of Frankfort gently slopes to the north, toward the main axis of the buried channel. A similar feature in the bedrock surface, but which slopes to the southwest, is present in the northeastern part of the region. These features probably represent tributaries to the main channel (Chelikowsky, 1976).

Stratigraphic relationships between the bedrock and glacial deposits are shown on the cross sections. Because of the sparseness of stratigraphic data, geologic contacts on the figures are only approximate. The Atchison Formation, which overlies bedrock in much of the area, is thin to absent (0 to 30 feet thick) to the southeast (Appendix B; Walters, 1954, plate 2; Ward, 1974, p. 9). Glacial till overlies the Atchison Formation at all locations.

The chert gravels along the axis of the channel were encountered in several wells, as shown on Table 4. Chert gravels were not found in any test
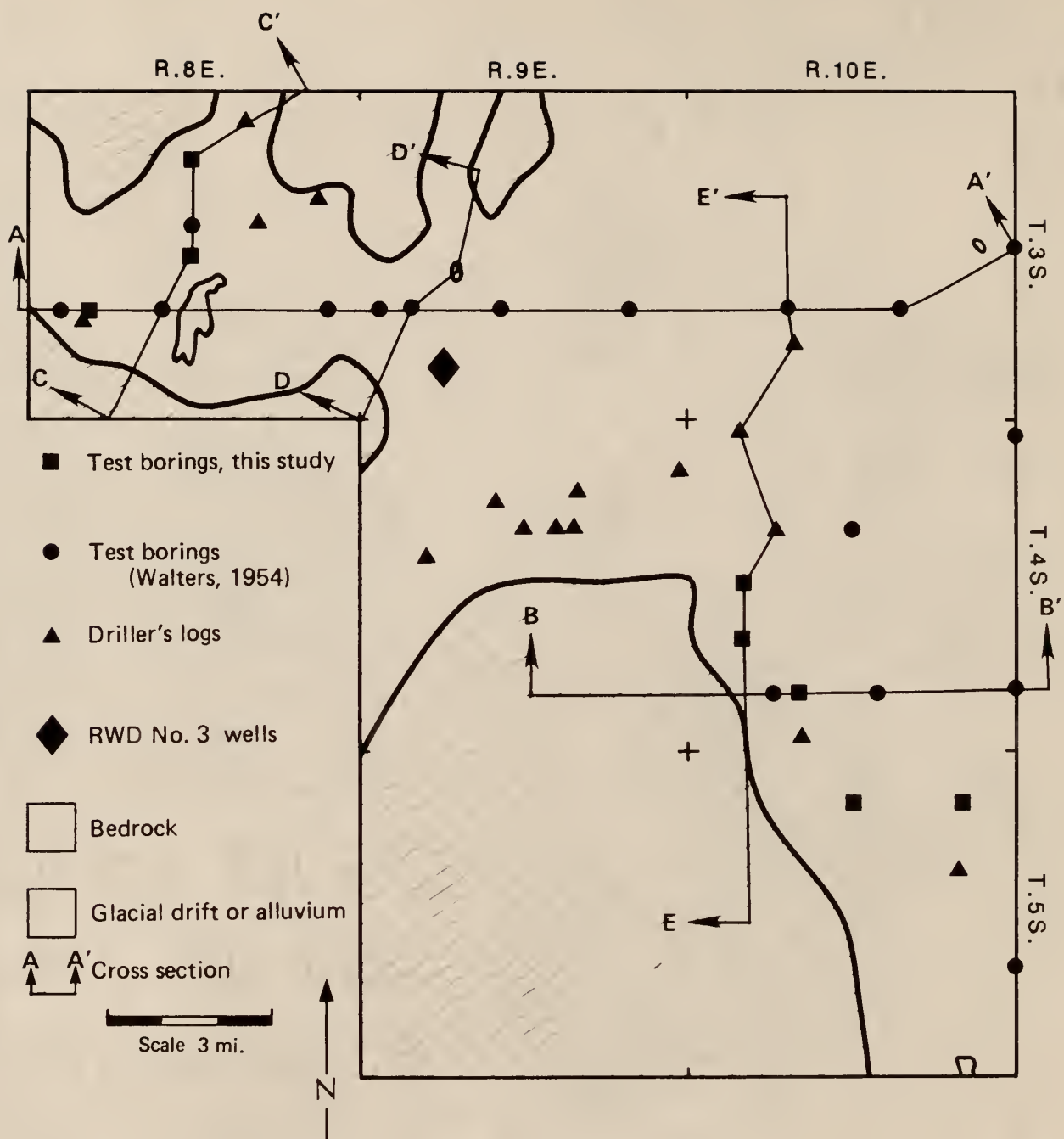
Figure 6 - **Locations of borings and wells encountering bedrock beneath glacial overburden**

Table 3.   Bedrock Elevations Beneath Glacial Overburden

Name	Location	Elevation, ft	Source
Wullschleger	3-8-3daa	1280	Driller's log
Test hole 3	3-8-9ada	1193	This study
Shellbaumer	3-8-13bab	1165	Driller's log
Vogelsburg	3-8-14bbd	1280	Driller's log
-	3-8-15bc	1158	Walters (1954)
Test hole 1	3-8-20ccc	1122	This study
Test hole 2	3-8-21aaa	1101	This study
-	3-8-25ba	1092	Walters (1954)
-	3-8-28ba	1291	Walters (1954)
D. Fincham	3-8-30aaa	1120	Driller's log
-	3-8-30ab	1281	Walters (1954)
-	3-9-19cd	1098	Walters (1954)
-	3-9-20cc	1064	Walters (1954)
-	3-9-26aa	1152	Walters (1954)
-	3-9-28ab	1148	Walters (1954)
RWD3, Well 1	3-9-32aba	1063	Driller's log
RWD3, Well 9	3-9-32aba	1078	Schwab/Eaton
RWD3, Well 3	3-9-32abb	1071	Driller's log
Test Well	3-9-32abb	1076	Beck (pers comm)
RWD3, Well 10	3-9-32abb	1077	Schwab/Eaton
RWD3, Well 6	3-9-32acb	1078	Schwab/Eaton
RWD3, Well 2	3-9-32baa	1077	Driller's log
RWD3, Well 5	3-9-32baa	1095	Schwab/Eaton
RWD3, Well 7	3-9-32baa	1071	Schwab/Eaton
RWD3, Well 4	3-9-32bab	1102	Schwab/Eaton
-	3-10-20dd	1165	Walters (1954)
-	3-10-22dd	1123	Walters (1954)
Van Dorn	3-10-28cbc	1119	Driller's log
-	3-11-18cc	1186	Walters (1954)
Maas	4-9-1ddd	1052	Driller's log
TH 1	4-9-2ccc	1069	Beck (pers comm)
TH 4	4-9-9acc	1080	Beck (pers comm)
TH 2	4-9-10dcc	1171	Beck (pers comm)
TH 3	4-9-10ddd	1119	Beck (pers comm)
TH 5	4-9-11bba	1040	Beck (pers comm)
Dunlap	4-9-11bbc	1055	Walters (1954)
Frankfort Municipal Golf Course	4-9-16aaa	1057	Beck (pers comm)
R. Feldhausen	4-9-17bcd	1081	Driller's log

Table 3. (continued)

-	4-10-1ad	1243	Walters (1954)
-	4-10-16aa	1041	Walters (1954)
J. Stiner	4-10-17ab	1038	Driller's log
Test hole 8	4-10-17ccc	1142	This study
Test hole 7	4-10-19ddd	1223	This study
-	4-10-25dd	1024	Walters (1954)
-	4-10-27cd	1071	Walters (1954)
Test hole 6	4-10-28ccc	1198	This study
-	4-10-29dc	1183	Walters (1954)
L. Hunninghake	4-10-33cc	1222	Driller's log
Glasgow 1	4-10-6dad	1040	Beck (pers comm)
Test hole 4	5-10-1ccc	1143	This study
Test hole 5	5-10-3ccc	1226	This study
M. Bramhall	5-10-14ada	1153	Driller's log
-	5-11-30bb	1192	Walters (1954)
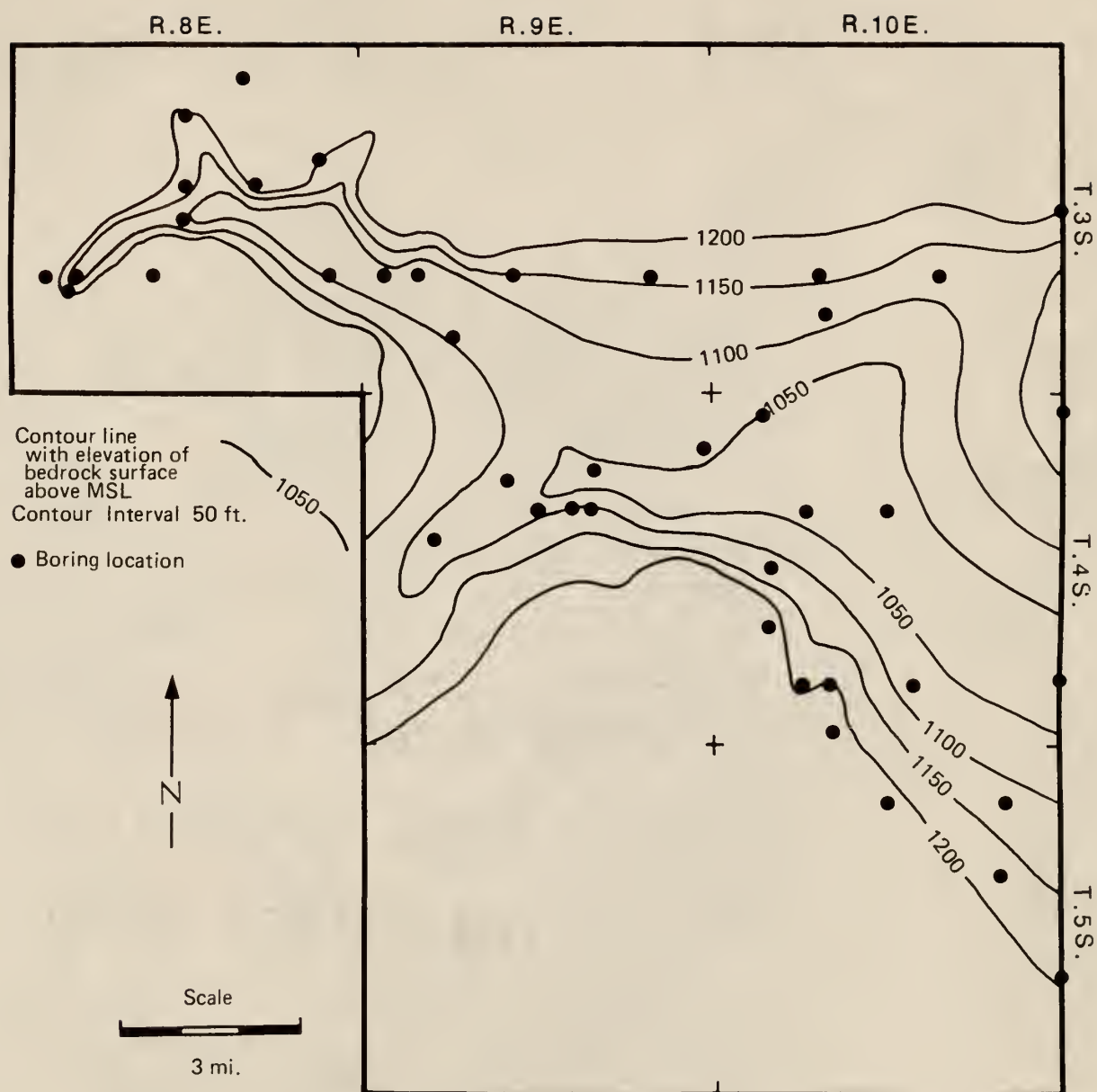
Figure 7 - **Contour map of bedrock surface beneath glacial deposits**
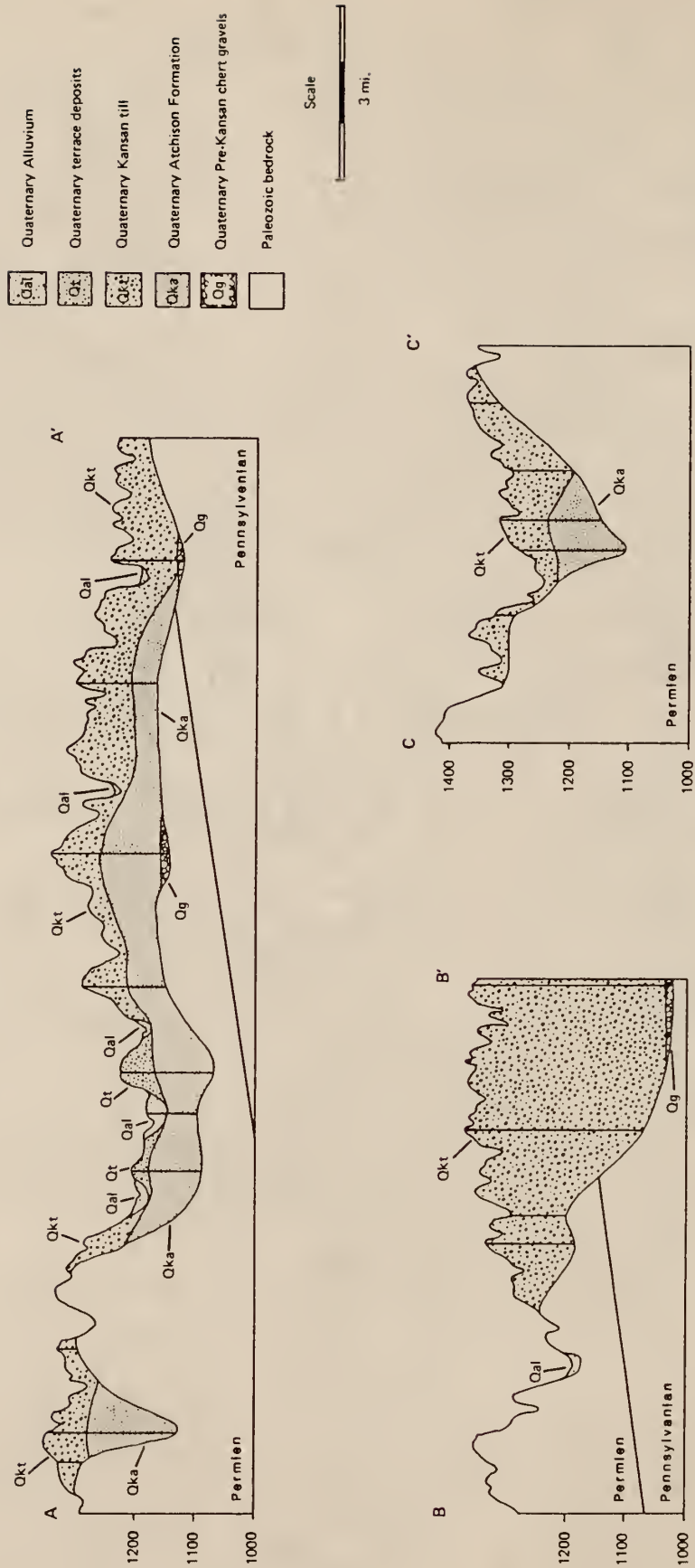
Figure 8 - Cross sections A-A', B-B', and C-C' (after Walters, 1954)

Figure 9 Cross sections D-D' and E-E' (after Walters, 1954)
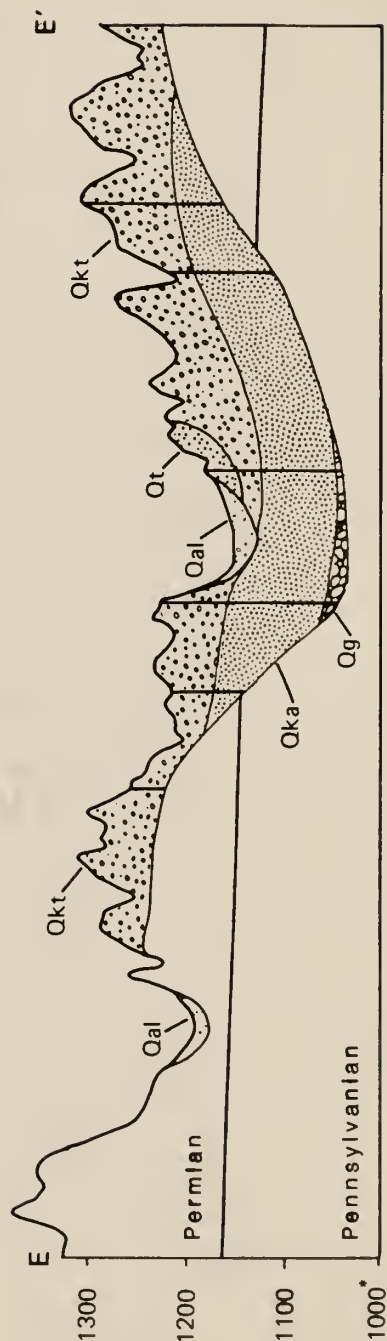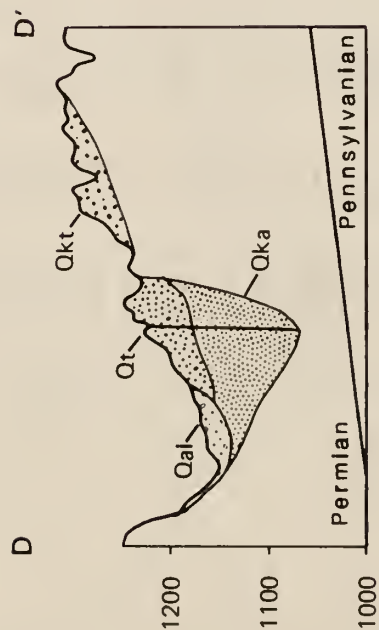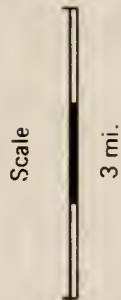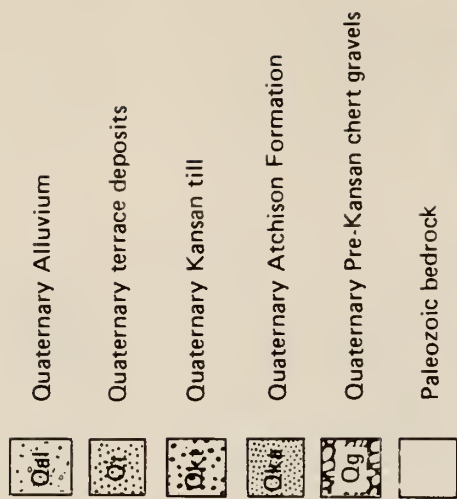
* Vertical scale in feet above Mean Sea Level

Table 4. Locations of Wells in Which Chert Gravels Were Encountered

Name	Location	Thickness of gravel, feet	Source
A. Maas	4-9-1ddd	22	Driller's log
J. Stiner	4-10-17ab	12	Driller's log
Van Dorn	3-10-28cbc	6	Driller's log
Dunlap	4-9-11bbc	22	Walters (1954)
RWD3 wells	3-9-32ab and ba	1-8	Driller's log and Schwab and Eaton report dated 1/26/77
Glasgow 1	4-10-6dad	15	Beck (pers comm)
Frankfort Golf Course Well #4	4-9-16aaa	12	Beck (pers comm)
Test Hole #1	4-9-2ccc	34	Beck (pers comm)
Test Hole #3	4-9-10ddd	4	Beck (pers comm)
Test Hole #4	4-9-9acc	8	Beck (pers comm)
Test Hole #5	4-9-11bba	>13	Beck (pers comm)
-	4-10-16aa	14	Walters (1954)
-	4-10-25dd	5	Walters (1954)
-	3-9-26aa	7.5	Walters (1954)
-	3-10-22dd	11.5	Walters (1954)
M. Bramhall	5-10-14ada	1	Driller's log

borings installed for this investigation. As shown on Table 4, maximum thickness of the gravels in the region is 20 to 30 feet. Ground-water yields from wells in the gravels are the largest in the area. Aquifer test information from driller's logs indicates yields up to 300 gpm are possible.

Water levels in wells completed in the chert gravels rise much above the top of the gravels, indicating that either ground water in the gravels is confined or there is good hydraulic connection with the overlying sands. Because the wells are generally constructed with a gravel pack extending to within 20 feet of ground surface, it is not possible to determine if these high water levels are due to a confined system. On the basis of geologic logs and similar water level elevations in several channel-wells (T.4 S., R.10 E., sec. 17ccc and T.4 S, R.9 E., sec. 1ddd, and T.3 S., R.9 E., sec. 32) which are located as much as seven miles apart, it appears that wells completed in the buried channel may be hydraulically connected. In addition, geologic logs for RWD3 wells indicate the alluvium of Robidoux Creek is probably hydraulically connected to the chert gravels, which occur on the bedrock surface.

Ground-water recharge to the buried channel probably originates in the alluvium of the Robidoux Creek near where the buried channel crosses under the river. The ground water then moves to the southeast in the general direction of the bedrock-surface gradient under the influence of hydraulic head. Other sources of recharge are probably present; however, it appears that infiltration of ground water through the alluvium of the Robidoux River Valley, and perhaps the Black Vermillion River Valley, are the major components of recharge to the buried channel.

Glacial Deposits

The occurrence and movement of ground water in glacial deposits is affected greatly by their heterogeneous stratigraphy. Water levels in wells in the glacial deposits are commonly in the range of 15 to 60 feet below ground surface. A review of well logs and interviews with well owners indicate the deeper water levels are in wells in upland areas.

Ground water generally moves through primary pore spaces of sandy and gravelly aquifers and through fractures in the fine-grained deposits. The primary porosity of fine-grained glacial deposits is generally high, but their low permeability limits ground-water velocities. As a result, ground-water yields from till are generally on the order of 10 gpm or less. Yields from the more permeable gravel aquifers can be 50 to 200 gpm (Ward, 1974, p. 11-14).

Ground-water recharge to glacial deposits occurs as infiltration of rainfall on upland areas or as underflow from bedrock or alluvium (Sharp, 1984). Because of its low permeability, little ground-water recharge occurs through the till; however, a considerable amount of recharge from rainfall may occur in areas underlain by glaciofluvial deposits (Ward, 1974, p. 11).

The fractures and joints in glacial till probably increase infiltration rates and can have a profound effect on ground-water recharge (Grisak and Cherry, 1975; Grisak et al., 1976; Sharp, 1984). Oxidation of the upper portion of the till to a depth of 20 to 45 feet (Appendix B) and along fractures is probably due to oxygenated recharge water passing through the till (Williams and Farvolden, 1967, p. 163). Because of its large outcrop area, the till probably contributes to some extent to ground-water recharge.

Ground-water discharge from the glacial deposits occurs in several ways, including evapotranspiration, discharge to streams, and deeper infiltration to bedrock or buried channel aquifers.

Alluvium

The alluvium along major stream valleys, such as the Black Vermillion and Robidoux river valleys, is generally saturated throughout its thickness. The water levels in wells along Robidoux Creek, including those of RWD3, are about 5-10 feet below ground surface based on well logs.

Ground water occupies and moves through the primary pore spaces of the alluvium. Sands and gravels of the alluvium are generally highly permeable and can easily transmit ground water. The driller's report for two wells approximately 50-60 feet deep and completed in the alluvium of the Robidoux River indicate an estimated yield of 600 gpm.

The direction of ground-water flow, particularly horizontal movement, is normally from the alluvium toward an adjacent river where it discharges (Walters, 1954, p. 22). At high stage or during a rise in river stage following a period of drought, ground water probably flows from the river into the alluvium. Ground water also moves vertically through the alluvium into underlying permeable deposits. The locally higher ground-water levels in bedrock or till aquifers probably results in ground-water movement into the alluvium (Whittemore et al., 1982, p. 18). The magnitude of this component of recharge is unknown.

HYDROGEOCHEMISTRY

Chemical Character of Hydrogeologic Units

Appendix C contains the results of all chemical analyses for samples collected from each hydrogeologic unit. Table 5 represents the range and median of ion concentrations and selected hydrochemical parameters for samples collected from each hydrogeologic unit. Median ion concentrations are also shown graphically in Figure 10. Three samples are omitted from these two statistical summaries because their charge balance error exceeded an acceptable 5%. The charge balance error for all other samples ranged between +3.3% and -3.0% with a mean of +0.47%.

The following discussion of specific chemical characteristics for each hydrogeologic unit is based on hydrochemical data contained in Appendix C, which includes the results of analyses and calculated hydrochemical parameters, and other historical hydrochemical data contained in Appendix D. The data in Appendix D were collected from literature sources and Kansas Department of Health and Environment (KDHE) and included for comparative purposes.

Bedrock.--The ground-water samples collected from bedrock show great geographic variation in total-dissolved-solids concentration (TDS), and are typical of ground water from carbonate terranes. The ground water from the bedrock is generally more highly mineralized than ground water from glacial deposits and the buried channel. The major cation is Ca, whereas the anions primarily consist of HCO_3 and SO_4. Thus, Ca-HCO_3-type water is predominant and Ca-SO_4-type water is also common. As shown in Figure 11, mixed water-types are also present, but are relatively uncommon.

Table 5. Range and Median of Ion Concentrations and Selected Hydrochemical Parameters for each Hydrologic Unit

Parameter	Buried Channel (10)			Glacial Deposits (31)			Bedrock (18)		
	Maximum	Median	Minimum	Maximum	Median	Minimum	Maximum	Median	Minimum
Ca	105	94	85	205	90	50	280	134	94
Mg	21	14	9.9	47	22	6.8	58	29	18
Sr	0.7	0.5	0.2	6.4	0.7	0.1	15	1.3	0.1
Na	49	30	18	104	36	19	61	31	5.7
K	2.1	1.7	1.2	7.4	2.0	0.7	2.2	0.9	0.1
HCO_3	450	400	320	480	370	230	590	390	350
Cl	21	8.8	3.8	88	12	3.6	46	16	4.7
SO_4	54	19	6.0	330	48	4.0	630	105	17
NO_3	5.4	0.9	0.1	125	1.2	0.1	83	41	0.1
pH	7.10	7.06	6.98	7.36	7.17	6.86	7.25	7.03	6.83
T, °C	15.4	14.3	12.8	16.2	14.3	12.5	17.0	13.8	11.9
SEC	810	670	550	1400	750	390	1700	920	620
TDS*	470	350	310	950	430	210	1220	950	350
P_{CO_2}	$10^{-1.5}$	$10^{-1.6}$	$10^{-1.6}$	$10^{-1.4}$	$10^{-1.6}$	$10^{-1.9}$	$10^{-1.3}$	$10^{-1.5}$	$10^{-1.8}$

Notes: Values in parentheses are the number of samples from each hydrogeologic unit; concentrations expressed in mg/L; SEC in micromhos/cm at 25°C.

* Computed as sum of constituents assuming 0.4917 (HCO_3)
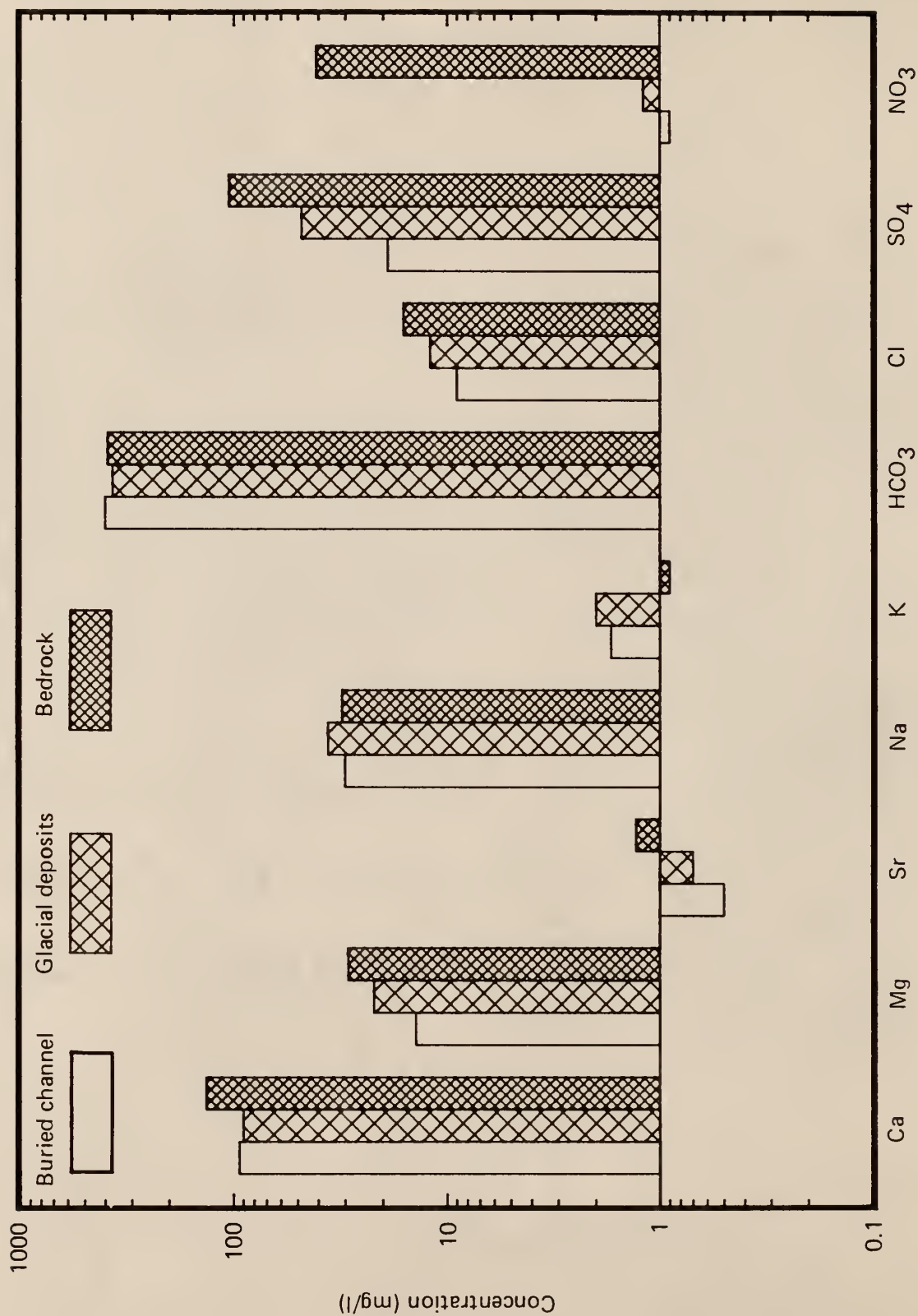
Figure 10 - Bar chart of median ion concentrations for ground-water samples from each hydrogeologic unit
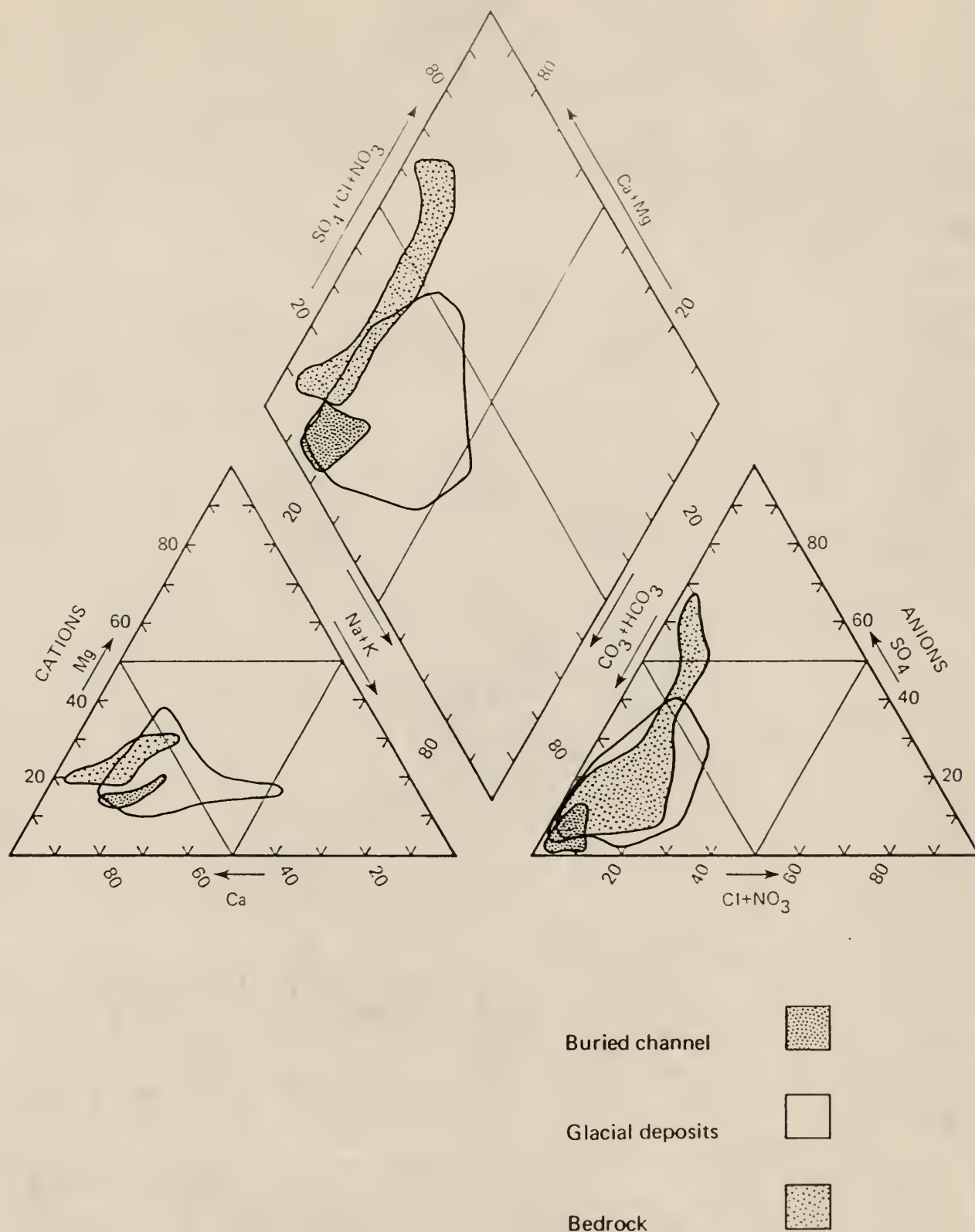
Figure 11 - **Trilinear diagram**

TDS ranges from 350 to 1220 mg/L, although Walters (1954, Table 3) reported values as high as 2000 mg/L. This wide range is primarily due to variations in concentrations of Ca and SO_4. The more highly mineralized waters are $Ca-SO_4$-type water, which usually contain greater than 250 mg/L SO_4 derived from solution of gypsum. Bicarbonate concentrations are also a major component of TDS, although the range of HCO_3 concentrations is much narrower than that for SO_4.

The concentrations of Na and K are lower than concentrations of Ca and Mg. The molal concentration of Na is much less than for Ca, but only slightly less than for Mg. Potassium concentrations are low as typical in ground waters, with most values below 1.5 mg/L. Strontium concentrations are highest in ground water from the bedrock. Concentrations are generally below 2 mg/L except in a few highly mineralized samples where values range up to 15 mg/L in a sample with 250 mg/L SO_4.

The molal concentrations of Cl are less than those of Na in nearly all samples. Nitrate concentrations are highly variable and exceed recommended drinking water standards of 45 mg/L as NO_3 (U.S. EPA, 1976) in 4 wells. The source of NO_3 to the ground water is probably from surface or near-surface runoff from barnyards or septic systems (Hem, 1985, p. 125). In many cases, shallow, old wells lack a surface cement seal, which permits relatively rapid infiltration of NO_3-contaminated surface water. The highest NO_3 concentration in bedrock wells is 83 mg/L in a well located near a livestock pen. The pH of ground water falls in a narrow range of values between 6.83 and 7.25 and is similar to the range of values in other hydrogeologic units.

Buried channel.--Ground water from the buried channel is less mineralized than ground water in the bedrock. Concentrations of TDS for the buried

channel waters range from 310 to 470 mg/L and are within the range of TDS for the glacial deposits. Samples collected from the buried channel are Ca-HCO$_3$-type water and contain generally similar ion concentrations. Molal concentrations of Mg and Na are about equal, but are less than Ca. The principal anion is HCO$_3$, which comprises greater than 80-90% of the molal content of the anion total, and is the largest single component of TDS. Nitrate concentrations are generally below 1 mg/L, probably because these wells are nearly 200 feet deep and were constructed with a sanitary seal within the last 10 years, minimizing the potential for contamination by surface waters. The pH of ground water is in the narrow range of 6.98 to 7.10.

Glacial Deposits.--Ground water in the glacial deposits is generally less mineralized than ground water in the bedrock and, in some cases, is also less mineralized than ground water in the buried channel. TDS ranges from 210 to 950 mg/L. The major cations are generally Ca and Mg. Molal concentrations of Na are higher than those of Mg in a number of samples and generally occur when concentrations of Ca, Mg, and TDS are quite low. Concentrations of Na and K are generally higher in ground-water samples from the glacial deposits than the other hydrogeologic units. The high K and Na values are probably the result of ion-exchange reactions involving the smectite clays, which are abundant in the glacial deposits, particularly the till. The major anions commonly consist of HCO$_3$ and SO$_4$. Molal concentrations of Cl are sometimes greater than SO$_4$, generally when Na concentrations are elevated. Most of the ground water is Ca-HCO$_3$-type water, but Ca-SO$_4$-type water was encountered in a few areas. Na-HCO$_3$-type water is also present, but is uncommon and could be derived from either surface contamination or natural processes. Dissolved NO$_3$ in the Na-HCO$_3$-type waters is low, ruling out typical surface contamination from animal or human wastes. However, Cl

contents tend to be higher for these waters than most other ground waters in the glacial deposits. Concentration of near surface waters by evapotranspiration, coupled with ion exchange in clays and associated carbonate mineral precipitation/solution in the deposits are the possible natural processes that might produce the $Na-HCO_3$-type waters.

The geographic variation in ion concentrations is generally less than for the bedrock aquifers, but is greater than in the buried channel deposits. Concentrations of most ions are within a narrow range with just a few samples having significantly higher or lower concentrations. The greatest variation in concentration is for NO_3, which ranges from less than 1 mg/L to 125 mg/L. As for the bedrock wells, the highest concentrations appear to be in shallow, old wells located near livestock pens.

Alluvium.--Because operating wells could not be located, ground-water samples from the alluvium were not collected as part of this investigation. Historical hydrochemical data contained in Appendix D and those of Walters (1954, p. 65) indicate that ground water in the alluvium is similar to ground water in the buried channel. Based on the available historical data, ground water in the alluvium is $Ca-HCO_3$-type water with TDS of about 300 mg/L.

Temporal Variations

Temporal variations in hydrochemistry due to seasonal climatic changes were evaluated for the different hydrogeologic units. Multiple ground-water samples were collected periodically from 12 wells between September 1982 and September 1983. The number of multiple samples collected from each well varied from 2 to 4. Additionally, historical hydrochemical data shown in Appendix D includes data from 1981 for two wells in the buried channel and one well in glacial drift.

The hydrochemical data contained in Appendixes C and D indicate that wells in the buried channel or glacial deposits sampled showed no systematic temporal variations in response to changes in wet or dry climatic conditions. The ion concentrations generally varied by no more than 5 to 10 percent between sample dates. Concentrations of Ca, Mg, and HCO_3 were particularly consistent and may reflect the effects of relatively rapid carbonate equilibria.

The relatively constant hydrochemistry of the buried channel waters is probably because the aquifer is deeply buried by several hundred feet of glacial drift. The time required for recharge waters to reach these deposits acts to buffer changes in the hydrochemistry. The absence of significant temporal changes in the hydrochemistry of the drift is related to the low ground-water velocities and slow recharge rate.

In contrast to ground water from the buried channel and glacial deposits, the ground-water samples from bedrock aquifers showed significant temporal variations in ion concentrations that could be related to seasonal effects. The greatest changes occurred in concentrations of SO_4, and to a lesser extent, Ca. The Forst multiple samples showed a decrease in SO_4 concentrations from 500 mg/L to less than 45 mg/L. The concentrations of other ions in these samples also decreased, but not by more than 50 percent. The SO_4 concentrations in the Alley samples also changed between sampling dates but by less than about 40 percent.

The change in hydrochemistry of the bedrock aquifers is probably because highly mineralized ground water is being diluted by recharge waters containing differing ion ratios. This effect is well documented in gypsum-bearing Permian limestone aquifers of northeast Kansas (Whittemore et al., 1982). The

large fractures common in these rocks probably enhance this dilution by permitting infiltration of relatively dilute recharge water during wet periods. The time for recharge to substantially dilute ground water pumped by the bedrock wells is estimated to be on the order of a few to several months (Whittemore, pers. comm.). Climatic data for the town of Frankfort several miles north of the bedrock wells with multiple samples show appreciable positive departures from normal precipitation during the study period (U.S. Dept. of Commerce, 1981, 1982, and 1983). Frankfort received about 1 inch of precipitation over the average in 1981 in contrast to an excess of over 13 inches during 1982. This record appears to fit with the dilution hypothesis.

Geochemistry of Waters

A comparison of the hydrochemistry of samples from each hydrogeologic unit suggests significant similarities in the geochemical processes affecting their hydrochemical evolution. Most ground waters in the investigation area are of $Ca-HCO_3$-type with subordinate concentrations of Mg, Na, Cl, and SO_4 (Fig. 11); however, a few have distinctly different chemical characteristics. The most obvious chemical differences are in the high SO_4 and NO_3 concentrations for some ground-water samples from bedrock and the variations in concentrations of Na, K, and NO_3 for waters in the glacial aquifers. These similarities and dissimilarities in hydrochemistry are generally a reflection of the bulk mineralogy of each aquifer system, except for NO_3, which is probably derived from a surface source of contamination.

As shown in Figure 11, the trilinear diagram, the fields representing the range of water composition for each hydrogeologic unit overlap to some degree. This overlap generally occurs where Ca and HCO_3 represent greater than 50% of the total cations and anions, respectively. The shapes and

patterns of the fields on the diagram were evaluated for possible mixing trends; however, no such trends are apparent in the data. The relationship between water type and TDS concentration was also evaluated. It appears that as TDS concentrations increase, there is an increase in the relative concentration of SO_4. Thus, most of the ground water with high TDS concentrations tend to be Ca-SO_4-type water, regardless of the hydrogeologic unit from which the sample was collected.

As suggested previously, the hydrochemical data collected for this investigation indicate that the hydrochemical evolution of the ground water is affected by dissolution or precipitation of carbonate minerals (e.g. calcite and dolomite), dissolution of sulfate minerals (e.g. gypsum), and ion exchange reactions involving smectite clays.

The following discussions of selected hydrochemical parameters and geochemical relationships between dissolved ions present evidence of the major sources and controls for the dissolved constituents in the ground water in each aquifer system.

Saturation indices.--The saturation index (SI) is defined for various solid phases as the log of the quotient of the ion activity product (IAP) divided by the equilibrium constant (K) (SI=log (IAP/K)). SI represents the equilibrium condition (undersaturated, saturated, or supersaturated) of a solution with respect to a given solid-water reaction and generally indicates whether the solid will tend to precipitate or dissolve in the solution. Evaluation of SI for selected minerals or other solids can help in understanding the processes that control the hydrochemical evolution of ground water, particularly the upper limit of concentration for certain dissolved ions.

Saturation indices for ground-water samples were calculated using the computer program WATEQF (Plummer et al., 1976). To calculate SI the program determined the chemical activity (a) of each ion in solution, ionic strength (I) of the solution, and IAP for selected reactions of interest. The equations for chemical activity and ionic strength are shown below.

Activity of ith ion, a_i -

$$a_i = \gamma_i \times m_i \tag{1}$$

where, γ_i = activity coefficient

m_i = molality of ith ion

Ionic strength of solution, I -

$$I = 0.5\sqrt{(C_i \times Z_i^2)} \tag{2}$$

where, C_i = molality of ith ion

Z_i = charge on the ith ion

The activity coefficients (γ_i) were calculated from the extended Debye-Huckel equation (Truesdell and Jones, 1974) shown below.

Activity coefficient of ith ion, γ_i -

$$\log \gamma_i = ((-AZ_i^2 \sqrt{(I)})/(1+Ba_i \sqrt{(I)}))+bI \tag{3}$$

where, A and B are dependent on dielectric constant, density, and temperature of the water and

     Z = charge on the ith ion,
     I = ionic strength of solution,
     a = size of hydrated ith ion,
     b = factor allowing for the effect of a decrease in concentration of
         the solvent (Truesdell and Jones, 1974).

The number and type of solid phases for which saturation indices were calculated is dependent on the analytical data provided to WATEQF. Although saturation indices were calculated for 20 solid phases, only those for calcite (SI_c), dolomite (SI_d), and gypsum (SI_g) were found to be relevant in

determining the controls on ion concentrations. The calculated SI for other solid phases indicated significantly undersaturated conditions, thus, they have virtually no impact on the upper limit of concentration for any dissolved ions. Because chemical analyses were not performed for selected constituents (e.g., silica), saturation indices for the commonly occurring clay minerals could not be calculated.

The equilibrium reactions used to represent precipitation or dissolution of calcite, dolomite, and gypsum are shown below (brackets indicate activity). The values of K shown below were obtained from WATEQF and are representative for waters at 25°C. The equilibrium constant is generally temperature dependent and appropriate corrections were made by WATEQF to account for the different ground-water temperatures.

Saturation index of calcite at 25°C, SI_c -

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{4}$$
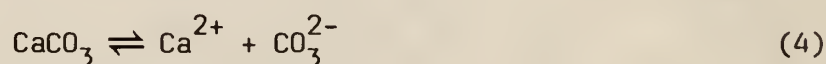
$$K_c = 10^{-8.47}$$

$$IAP_c = [Ca^{2+}] \times [CO_3^{2-}]$$

$$SI_c = \log \left(\frac{IAP_c}{K_c}\right)$$

Saturation index of dolomite at 25 C, SI_d -

$$CaMg(CO_3)_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + 2CO_3^{2-} \tag{5}$$
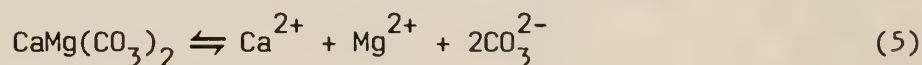
$$K_d = 10^{-17.02}$$

$$IAP_d = [Ca^{2+}] \times [Mg^{2+}] \times [CO_3^{2-}]^2$$

$$SI_d = \log \left(\frac{IAP_d}{K_d}\right)$$

Saturation index of gypsum at 25°C, SI_g -

$$CaSO_4 \bullet 2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O \tag{6}$$
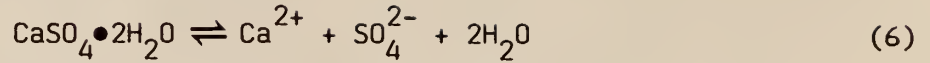
$$K_g = 10^{-4.76}$$

$$IAP_g = [Ca^{2+}] \times [SO_4^{2-}]$$

$$SI_g = \log \left(\frac{IAP_g}{K_g}\right)$$

Uncertainties in the values for concentration and activity coefficient for each component, thermochemical data, and pH, result in an uncertainty in the estimate of SI. SI_c and SI_d are particularly sensitive to errors in pH measurement. An error in pH measurement of 0.1 corresponds to an error of 0.1 for SI_c or SI_d. The pH used in calculation of SI_c and SI_d was measured in the field at the time of sample collection. It is generally assumed that the total uncertainty in SI_c and SI_d from all sources is about 0.1 units for good quality data (Langmuir, 1971, p. 1029). The uncertainty for SI_d may be slightly higher because of disagreement about the correct equilibrium constant for dolomite dissolution. Ground water with SI values within 0.1 units of zero are considered to be at saturation with respect to that solid phase.

The SI_c, SI_d, and SI_g for ground-water samples collected from each hydrogeologic unit are shown in Tables 6, 7, and 8. The range and median of the SI data are shown in Table 9. The median SI_c for all ground waters is between -0.10 and +0.04 and indicates saturation with respect to calcite. The median SI_d ranges from a low of -0.67 for the buried channel waters to a high of -0.31 for water from bedrock, indicating undersaturation with respect to dolomite. The higher SI_c relative to SI_d indicates that ground water

Table 6. Saturation Indices for Calcite, Dolomite, and Gypsum
for Ground-Water Samples from Bedrock

Name	Sample Date	SI_c	SI_d	SI_g
B. Alley	7/18/82	0.11	-0.15	-1.25
B. Alley	1/13/83	0.05	-0.25	-1.32
B. Alley	6/11/83	0.07	-0.32	-1.51
E. Ewing	7/18/82	0.15	-0.10	-0.60
E. Ewing	1/13/83	-0.04	-0.51	-0.70
E. Ewing	6/11/83	-0.02	-0.39	0.61
E. Ewing	9/ 9/83	0.11	-0.16	-0.80
V. Forst	7/18/82	0.15	-0.33	-0.42
V. Forst	6/11/83	-0.08	-0.79	-2.03
V. Forst	9/ 9/83	-0.09	-0.83	-1.63
D. Bonjour	6/23/83	0.19	-0.02	-1.17
H. Haskin	6/25/83	-0.03	-0.59	-1.76
W. Surdez	6/30/83	0.27	0.01	-1.27
R. Koch	6/11/83	-0.06	-0.68	-1.51
J. Wapp	6/11/83	0.09	-0.31	-0.36
D. Fincham*	7/ 5/83	-0.15	-0.92	-1.29
M. Samuelson	6/30/83	0.22	0.14	-0.88
L. Boeckman	7/ 5/83	-0.08	-0.41	-1.71

* Outside investigation area.

Table 7. Saturation Indices for Calcite, Dolomite, and Gypsum
for Ground-Water Samples from Glacial Deposits

Name	Sample Date	SI_c	SI_d	SI_g
J. Horigan	9/25/82	N/A	N/A	N/A
J. Horigan	1/13/83	0.08	-0.36	-1.34
J. Horigan	6/ 8/83	0.07	-0.41	-1.45
C. Swick	9/25/82	N/A	N/A	N/A
C. Swick	1/13/83	N/A	N/A	N/A
H. Huddleston	9/25/82	0.04	-0.61	-2.06
H. Huddleston	6/ 8/83	0.00	-0.64	-1.99
M. Bramhall	10/3/82	-0.27	-0.95	-2.48
M. Bramhall	6/23/83	-0.08	-0.52	-2.28
G. Feldhausen	2/19/83	-0.34	-1.40	-2.84
G. Feldhausen	6/23/83	-0.31	-1.30	-2.82
J. Sanderson	2/19/83	-0.15	-0.53	-1.54
J. Sanderson	6/ 8/83	-0.29	-0.80	-1.51
L. Baker	6/23/83	0.40	0.34	-0.68
D. Schooler	6/23/83	-0.18	-1.08	-1.93
K. Lindsey	6/23/83	-0.06	-0.92	-1.86
W. Foley	6/23/83	0.04	-0.27	-1.65
B. Bramhall	6/25/83	-0.01	-0.68	-2.19
W. Hanzlik	6/25/83	0.25	-0.01	-1.69
L. Wenzl	6/25/83	0.03	-0.25	-2.01
J. Boyle	6/25/83	0.22	0.08	-1.67
C. Seematter	6/25/83	0.03	-0.45	-1.59
D. Stock	6/30/83	0.16	0.19	-1.42
L. Ladner	6/30/83	0.14	-0.07	-1.35
H. Wullschleger	6/30/83	-0.06	-0.45	-1.61
B. Bliss	6/ 8/83	-0.13	-0.64	-2.27

Table 7 (continued)

Name	Sample Date	SI_c	SI_d	SI_g
D. Fincham	6/ 8/83	-0.09	-0.48	-1.47
C. Stiner	6/11/83	0.10	-0.15	-1.86
L. Millenbruch	6/30/83	0.23	0.13	-0.92
J. Vogelsburg	6/30/83	0.04	-0.40	-1.63
E. Foley	7/ 5/83	-0.13	-0.53	-1.55
G. Norman	7/ 5/83	-0.17	-0.71	-2.08
L. Ketter	7/ 5/83	-0.07	-0.64	-1.56
A. Argo	7/ 5/83	-0.16	-0.82	-0.99

Table 8. Saturation Indices for Calcite, Dolomite, and Gypsum
for Ground-Water Samples from the Buried Channel

Name	Sample Date	SI_c	SI_d	SI_g
A. Maas	9/25/82	-0.15	-1.04	-2.51
A. Maas	1/13/83	-0.14	-1.05	-2.20
A. Maas	6/ 8/83	-0.10	-0.97	-2.28
A. Maas	9/ 9/83	-0.06	-0.85	-2.23
L. Gerstner	1/13/83	-0.02	-0.68	-1.87
L. Gerstner	6/ 8/83	-0.07	-0.86	-1.87
L. Gerstner	9/ 9/83	0.10	-0.52	-1.88
J. Dunlap	6/ 8/83	-0.01	-0.51	-1.58
J. Stiner	6/11/83	-0.02	-0.67	-2.26
J. Stiner	9/ 9/83	-0.01	-0.65	-2.15

Table 9. Range and Median of SI and percent saturation for calcite, dolomite, and gypsum for ground-water samples

	SI_c			SI_d			SI_g		
	Maximum	Median	Minimum	Maximum	Median	Minimum	Maximum	Median	Minimum
Buried channel	+0.10 (126)	-0.05 (89)	-0.15 (71)	-0.51 (31)	-0.67 (21)	-1.05 (9)	-1.58 (3)	-2.03 (1)	-2.51 (<1)
Glacial deposits	+0.40 (250)	-0.10 (79)	-0.34 (46)	+0.34 (220)	-0.48 (33)	-1.40 (4)	-0.68 (21)	-1.65 (2)	-2.84 (<1)
Bedrock	+0.27 (186)	+0.04 (110)	-0.15 (71)	+0.14 (140)	-0.31 (49)	-0.92 (12)	-0.36 (44)	-1.27 (5)	-2.03 (1)

Percent saturation is shown in parentheses.

in the investigation area is closer to saturation with respect to calcite than dolomite.

The SI_c, SI_d for bedrock waters are similar to those of Whittemore and Switek (1977) for spring waters issuing from bedrock of the Council Grove Group in Pottawatomie County. The median SI_c and SI_d calculated for this investigation are +0.04 and -0.31, respectively, compared to -0.02 and -0.25 for the Pottawatomie County investigation. In general, the ranges of SI_c and SI_d were slightly wider for this investigation than those reported for the spring waters. These small deviations are within 0.1 and may be the result of slight differences in the thermodynamic data used to calculate SI_c and SI_d or small variations in analytical accuracy.

Figure 12 is a scatter plot of SI_c vs SI_d. Calcite and dolomite saturation fields shown on Figure 12 are based on the uncertainty in SI_c and SI_d of ±0.1 unit. The distribution of data points indicates that SI_c and SI_d generally increase in a similar manner. The data for the buried channel ground water are generally within the calcite saturation region and are low in SI_d for a given SI_c. The samples from bedrock and glacial deposits generally have a wider range of SI_c and SI_d than samples from the buried channel. The lowest SI_c and SI_d values are for ground water from the glacial deposits, whereas the highest values are similar in both hydrogeologic units.

The slope of a least squares line through the data is slightly less than the slope of the $SI_c = SI_d$ line (Fig. 12). The trend of these data show that as SI_c increases there is an even greater relative increase in SI_d. The ground waters with the highest SI_c (0.2 to 0.3) are almost equally supersaturated with respect to dolomite. This is probably because Ca has been
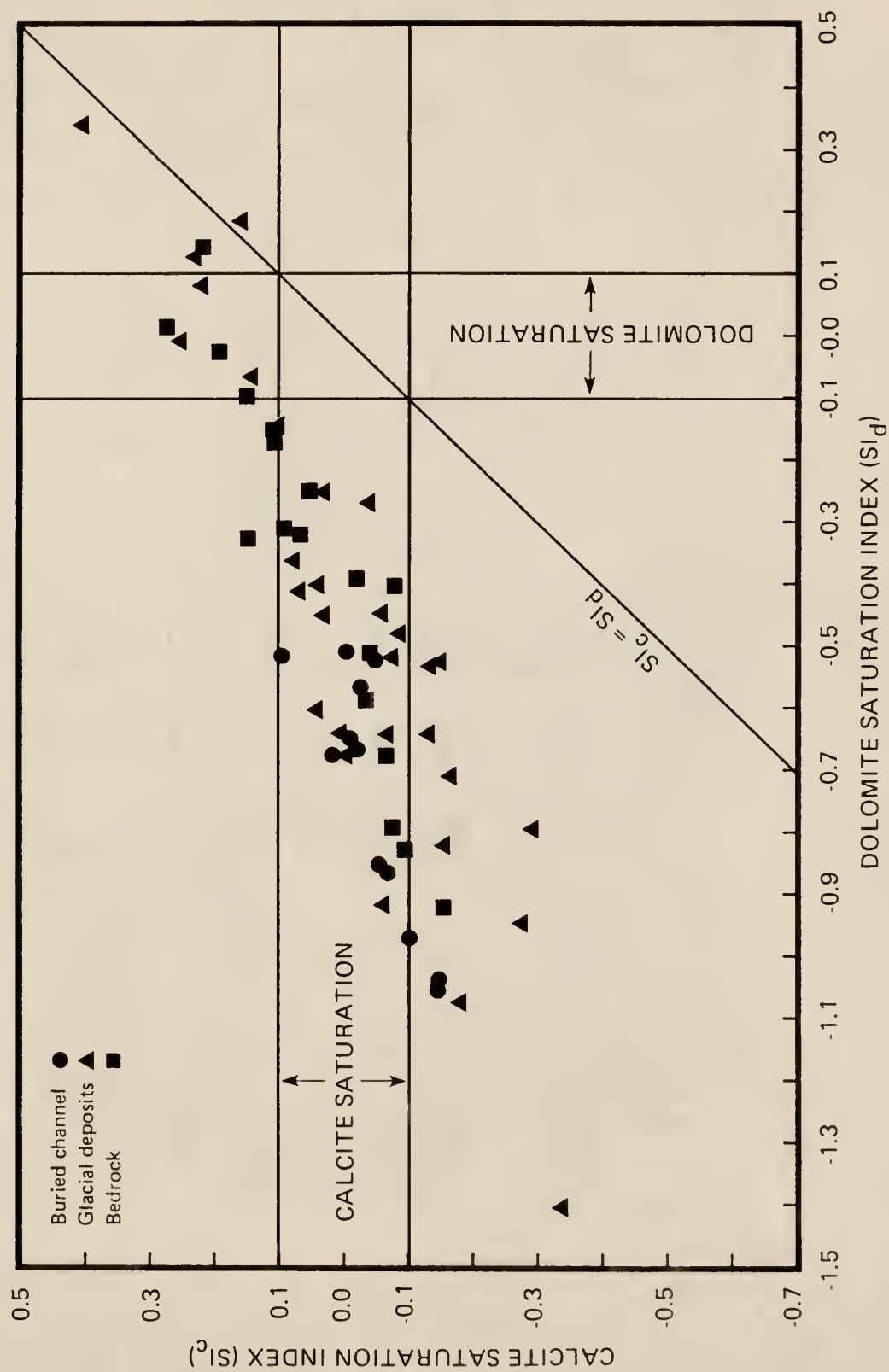
Figure 12 Scatter diagram of SIc vs SId (after Langmuir, 1971)

selectively removed from solution by precipitation of calcite resulting in a gradual relative increase in Mg, which results in the greater relative increase in SI_d.

The maximum values for SI_c and SI_d indicate slight supersaturation, which is not uncommon in some hydrogeologic systems. In regions where gypsum is abundant, supersaturation with respect to calcite can be maintained because of the relative rates of gypsum dissolution (faster) and calcite precipitation (slower). The high SI_c and SI_d for some of the samples is possibly due to mixing of hydrochemically dissimilar ground waters at the time of sample collection (Runnells, 1969).

Ground-water samples are significantly undersaturated with respect to gypsum, as shown on Table 9. The median SI_g for all samples is between -2.03 and -1.27. These values indicate about 1 to 5 percent saturation with respect to gypsum. The samples from bedrock had the highest overall levels of gypsum saturation, while samples from the buried channel had the lowest. The maximum SI_g of -0.36 was in a ground-water sample from bedrock containing 270 mg/L Ca and 630 mg/L SO_4. The higher SI_g values in ground water from the bedrock are probably due to the relative abundance of gypsum in subsurface bedrock formations (Walters, 1954; Amoco, 1975).

Partial Pressure of CO_2.--The partial pressure of CO_2 (P_{CO_2}) in the soil environment and the ground water exerts a strong influence on mineral-water reactions (Paces, 1971; Trainer and Heath, 1976; Freeze and Cherry, 1979, p. 240). The P_{CO_2} of ground water in equilibrium with atmospheric CO_2 is $10^{-3.5}$ atmospheres (atm); however, the soil environment commonly contains elevated P_{CO_2} levels from aerobic decay of organic matter and respiration of plant roots (Freeze and Cherry, 1979). Oxidation of

organic matter in aquifer sediments also can supply CO_2. These elevated

levels of CO_2 increase ground-water reactivity by decreasing pH and

increasing carbonic acid concentration. Equations 7 and 8 show the reactions

between CO_2 and water to form carbonic acid (H_2CO_3), which results in

increased reactivity of the ground water.

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3 \tag{7}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{8}$$
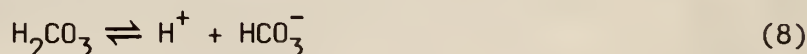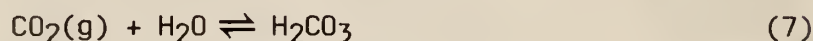
Ground-water samples collected for this investigation had calculated

P_{CO_2} levels in the narrow range of $10^{-1.9}$ to $10^{-1.3}$ atm (Table 5 and

Appendix C). This range is about 100 times greater than atmospheric P_{CO_2},

which is typical for some shallow ground-water systems (Paces, 1971, p. 237;

Grisak et al., 1976, p. 233; Freeze and Cherry, 1979, p. 241). The P_{CO_2}

values are similar in samples from all hydrogeologic units. Temporal changes

in P_{CO_2} are not apparent in the multiple samples, regardless of any changes

in TDS.

The hydrochemistry of the ground-water samples suggests open or near-open

conditions with respect to replenishment of CO_2. Waters with varying

degrees of saturation with respect to the carbonate minerals (e.g. calcite)

should theoretically show certain systematic variations in pH and HCO_3

depending on whether or not the ground-water system is open or closed with

respect to CO_2 replenishment (Langmuir, 1971). Ground water evolving under

closed-system conditions will generally have a higher pH and lower HCO_3 at

equilibrium than waters evolving under open-system conditions (Freeze and

Cherry, 1979, p. 255). A final pH of 7 is common for ground water evolving

to saturation with calcite or dolomite under open-system conditions (Freeze

and Cherry, 1979, p. 261). The hydrochemistry of ground waters in southeast

Marshall County, particularly the elevated P_{CO_2}, final pH near 7, and fairly consistent HCO_3 concentrations, indicate open or near-open conditions. However, certain of the expected systematic changes may be obscured by the relatively narrow range of values for pH and HCO_3.

Ca/Mg molal ratio.--The Ca/Mg molal ratio (Ca/Mg) has been shown to be related to aquifer mineralogy and can be useful in understanding the hydrogeochemistry of aquifer systems (Meisler and Bechler, 1967; Hem, 1970). Aquifers consisting mainly of calcite generally have the highest Ca/Mg for ground-water in carbonate terrains, whereas the lowest ratios are commonly found in dolomite aquifers. A Ca/Mg near unity is common in dolomite aquifers. Geochemical factors that can obscure this relationship include calcite precipitation (decreases Ca/Mg), different relative rates of dissolution of calcite and dolomite (variable effects), gypsum dissolution (increases Ca/Mg), and ion-exchange reactions between clays and the ground water involving Ca or Mg for Na or K (variable effects). Minor mineralogical impurities in the aquifers can also have a relatively large impact on the Ca/Mg, particularly if the minerals, such as gypsum, are highly soluble (Freeze and Cherry, 1979, p. 256).

The Ca/Mg of ground-water samples collected for this investigation ranges from about 1.2 to 5.6 (Fig. 13). Ground water from the buried channel aquifer had the highest Ca/Mg, generally between 4 and 5, and was geographically invariant. Samples from bedrock or glacial deposits had a much wider range of values and a larger degree of regional variation than did samples from the buried channel. Nearly all samples from the bedrock and glacial deposits had a Ca/Mg between 1.5 and 4. A few samples from the glacial deposits with low Mg concentrations (less than 10 mg/L) had a Ca/Mg greater than 4. The wide range of values for ground-water samples from bedrock and glacial deposits is
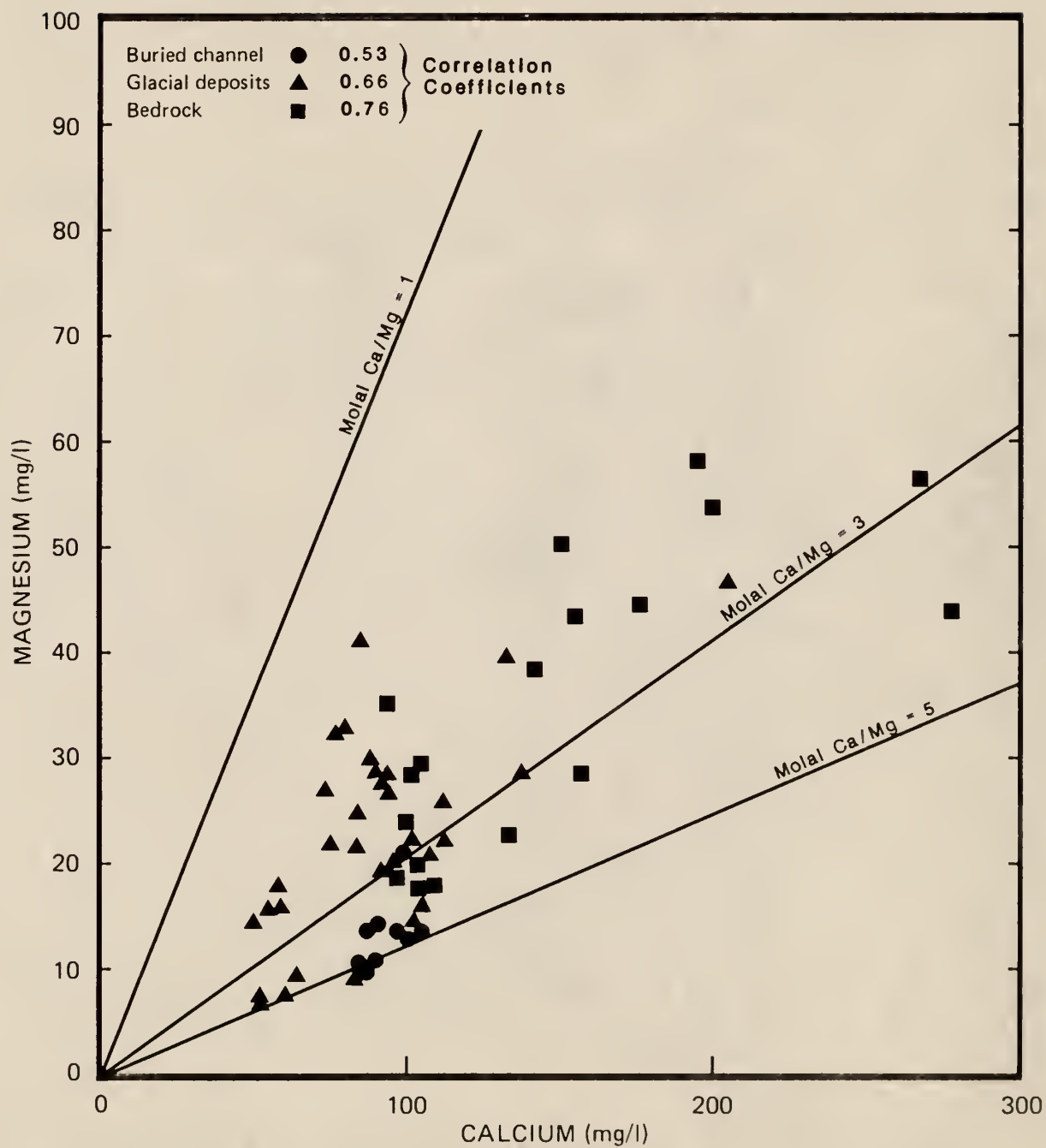
Figure 13 - **Scatter diagram of Ca vs Mg**

probably due to regional variations in aquifer mineralogy or differential solution or precipitation, whereas these factors do not appear to influence the Ca/Mg of ground water in the buried channel.

The relationships between Ca/Mg and SO_4 concentration for the ground-water samples are shown on Figure 14. The figure clearly shows that the highest Ca/Mg is found in samples from the buried channel and glacial deposits with low SO_4 concentrations. The Ca/Mg tends to decrease with increasing SO_4 up to about 200 mg/L SO_4, then appears to gradually increase with even higher SO_4 concentrations, reflecting the greater effect of gypsum solution.

In samples undersaturated with calcite, the dissolution of gypsum should increase the Ca/Mg of the ground water. However, these samples are generally slightly supersaturated with respect to calcite. Thus, the generally lower Ca/Mg suggests that Ca is being removed by calcite precipitation. Also, the high Ca concentrations could lead to changes in cation ratios from ion exchange on clays. The relatively low Ca/Mg of some ground-water samples from the glacial deposits, which also contain low concentrations of SO_4, may be due to the dissolution of dolomite that is commonly present in these rocks (Grisak et al, 1976, p. 322).

The Ca/Mg remained nearly constant in the multiple samples collected from selected wells regardless of changes in TDS. The Ca/Mg is probably constant because decreases in TDS were the result of dilution of the ground water by recharge water low in TDS, which could have only a minor impact on ion ratios. Ground water with large increases in SO_4 concentrations should have a consequent increase in the Ca/Mg due to the large influx of Ca from the dissolving gypsum; however, this was not observed in multiple samples
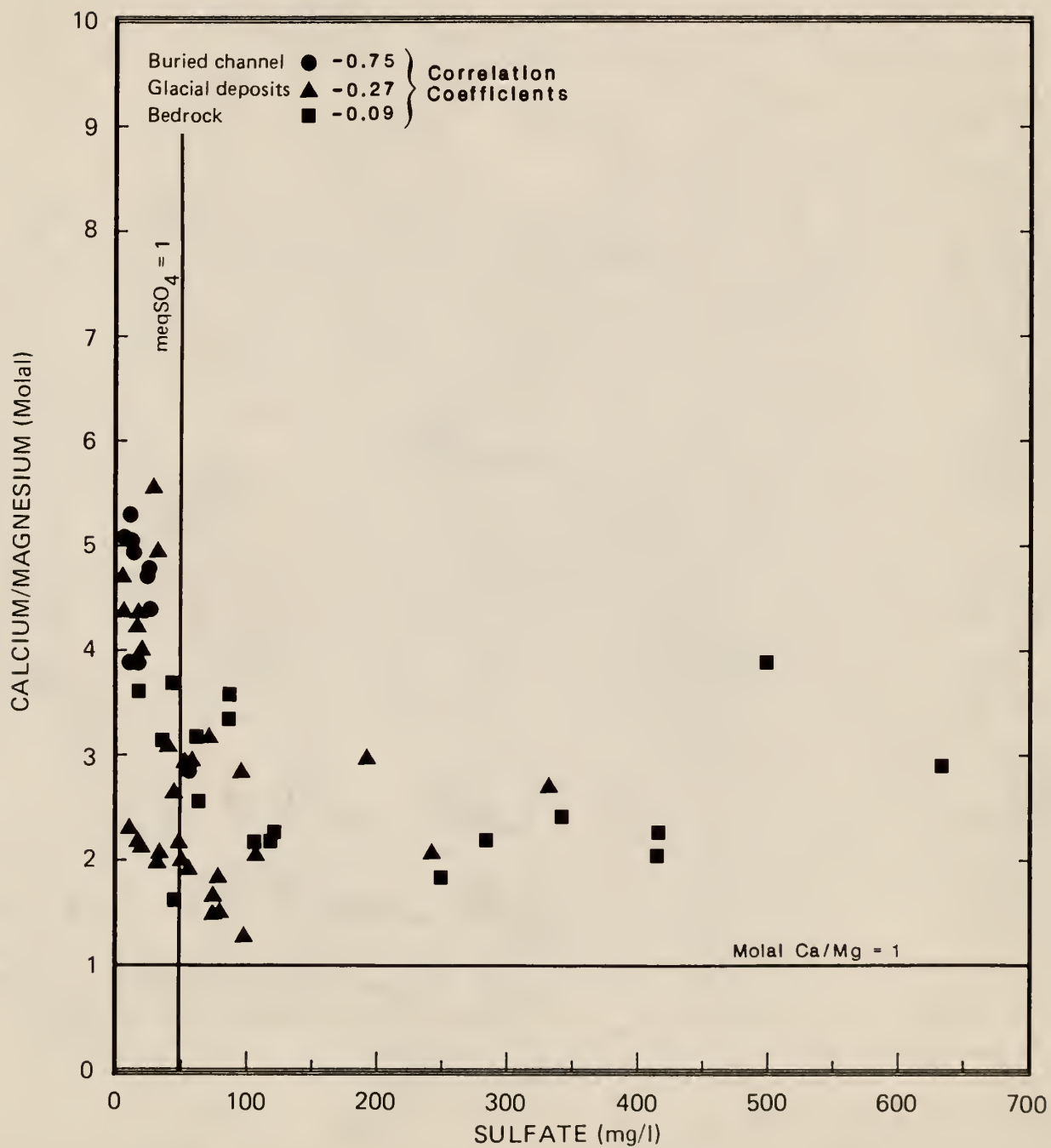
Figure 14 · **Scatter diagram of Ca/Mg vs SO₄**

displaying large increases in SO_4 concentration. Thus, increases in SO_4 are due more to less dilution by recharge than to increased solution of gypsum.

Ca vs HCO3.--The molal concentration of HCO_3 is greater than that of Ca in essentially all ground-water samples (Fig. 15). The Ca/HCO_3 molal ratio (Ca/HCO_3) is less than 0.5 in most samples, but increases as the concentration of SO_4 increases, reflecting the influence of gypsum dissolution on Ca/HCO_3. The greatest Ca/HCO_3 is observed in samples with SO_4 concentrations exceeding 500 mg/L.

The data for ground-water samples from the buried channel and glacial deposits generally show good correlation between concentrations of Ca and HCO_3, and appear to follow the trend for the dissolution of calcite, as shown below.

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^- \tag{9}$$
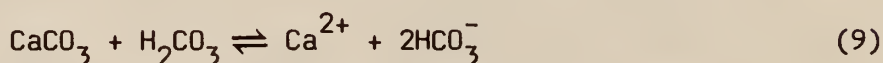
The theoretical Ca/HCO_3 for this reaction is 0.5 (Equation 9 and Figure 15). Ground-water samples from the buried channel and glacial deposits have Ca/HCO_3 in the range of approximately 0.3 to 0.5. The relationships between Ca and HCO_3 and the range of values of Ca/HCO_3 suggest that the dissolution of Ca-rich carbonate minerals plays a primary role in the hydrochemical evolution of these waters. The observed deviation from the theoretical Ca/HCO_3 of 0.5 is the result of the Mg content of the dissolving calcite (Equation 10) or, more importantly, by the dissolution of dolomite (Equation 11). The Mg addition causes an apparent decrease in the Ca/HCO_3 from the theoretical, as is generally observed in the samples from the buried channel and glacial deposits.

$$(Ca_x, Mg_{1-x})CO_3 + H_2CO_3 \rightleftharpoons Ca_x^{2+} + Mg_{1-x}^{2+} + 2HCO_3^- \tag{10}$$
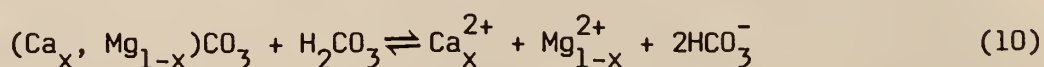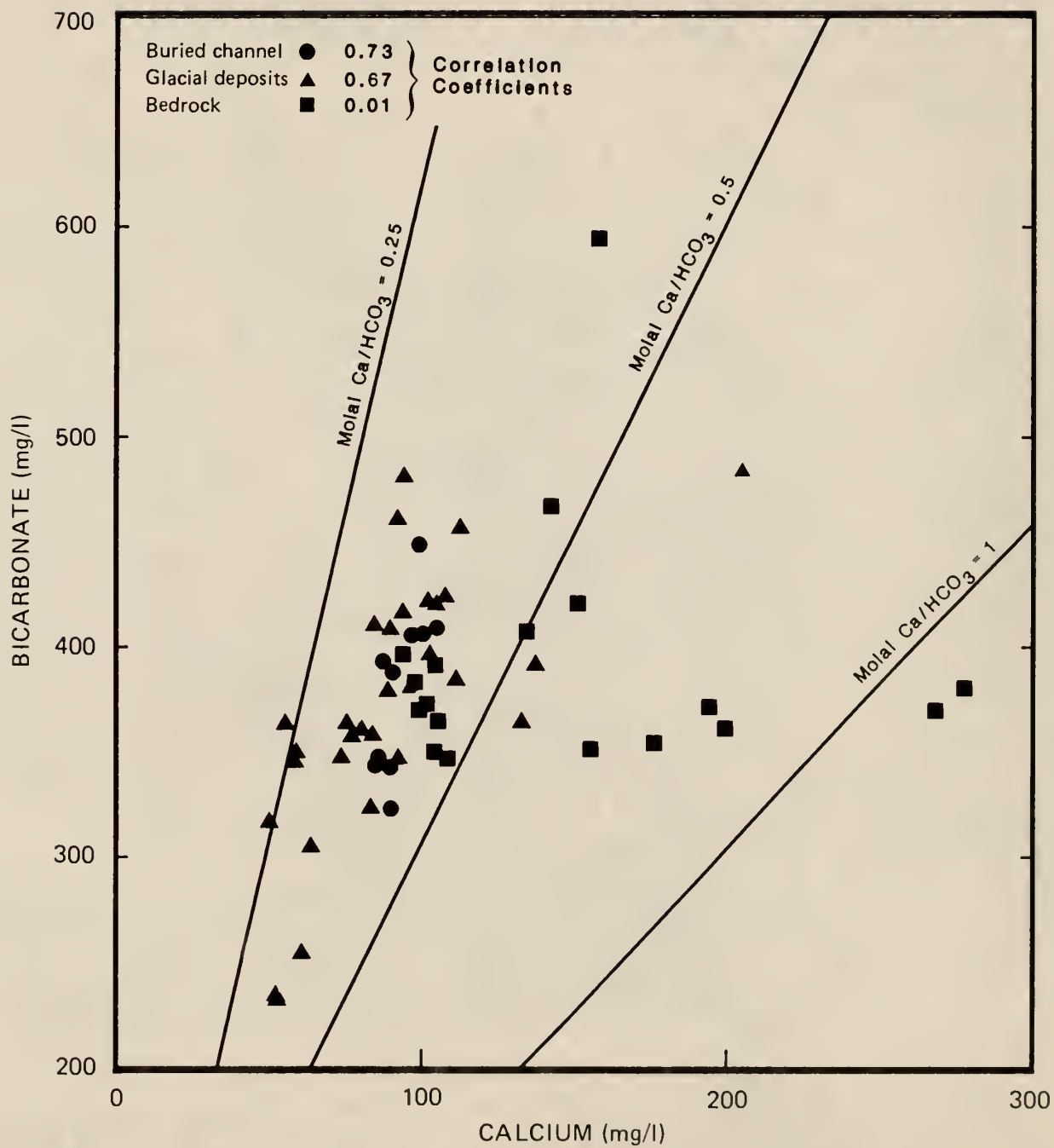
Figure 15 - **Scatter diagram of Ca vs HCO3**

$$Ca,Mg(CO_3)_2 + 2H_2CO_3 \rightleftharpoons Ca^{2+} + Mg^{2+} + 4HCO_3^- \tag{11}$$
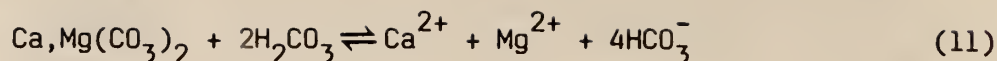
The Ca/HCO_3 in bedrock waters is generally greater than 0.5 and in some cases is greater than 1. The data for the bedrock waters have a large degree of scatter, particularly along the Ca axis. Based on SO_4 concentrations of greater than 125 mg/L, these ground-water samples appear to be affected greatly by the dissolution of gypsum, which also increases Ca and, thus, increases Ca/HCO_3 ratios.

Ca vs SO4.--The concentrations of Ca and SO_4 are positively correlated (Fig. 16). Concentrations of these ions are greatest in samples from the bedrock. The lowest SO_4 values are consistently found in the buried channel.

The molal concentrations of Ca exceed those of SO_4 in all samples. Samples with the lowest SO_4 concentrations have the greatest Ca/SO_4 molal ratio (Ca/SO_4). The Ca/SO_4 generally decreases as concentrations of Ca and SO_4 increase, approaching unity in samples with SO_4 concentrations greater than about 300 mg/L. As the concentration of Ca increases from the dissolution of gypsum, Ca is removed from solution by precipitation of calcite. Ion exchange reactions with the smectite clays in the glacial till could also remove Ca as the concentrations become greater (Freeze and Cherry, 1979, p. 286). The decreased Ca/SO_4 is the result of this preferential removal of Ca relative to SO_4.

The relatively high concentrations of SO_4 in ground water from Permian bedrock aquifers and the relatively low concentrations of SO_4 in ground water from the buried channel suggest that only minor ground-water recharge to the buried channel is occurring as underflow from the bedrock. If a large proportion of this ground-water recharge was being received as underflow from

Figure 16 - **Scatter diagram of Ca vs SO4**
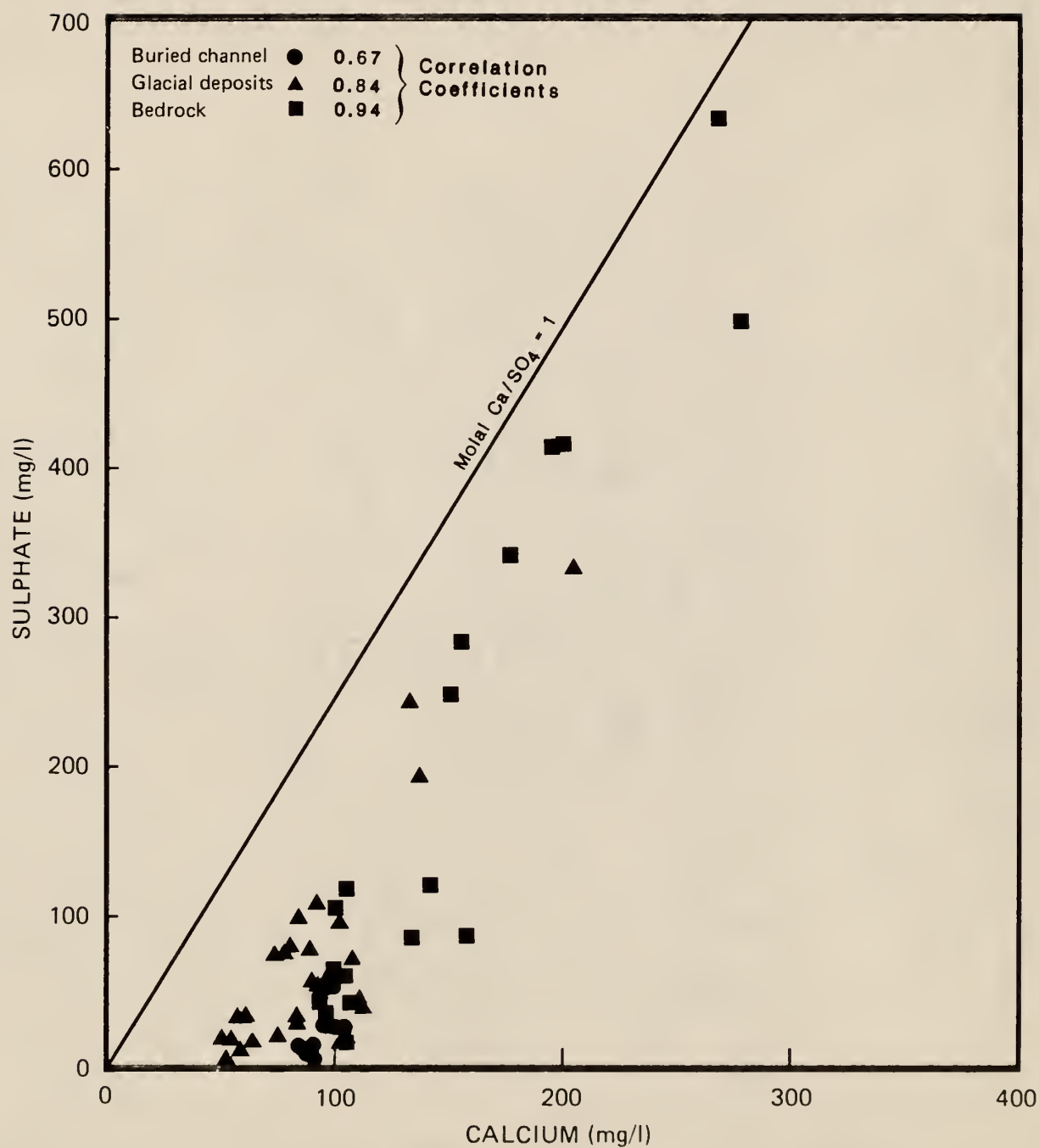
bedrock aquifers, the SO_4 concentrations in at least some ground water from the buried channel would probably have higher SO_4 concentrations than those observed. Ward (1974) found SO_4 concentrations greater than 1500 mg/L in the buried channel in Nemaha County, suggesting that in certain areas a large proportion of ground-water recharge to the buried channel originates as underflow from the Permian bedrock (Ward, 1974, p. 19). Recharge to the buried channel could be occurring from the bedrock where the ground water has low SO_4 concentrations, such as the Pennsylvanian bedrock along the eastern edge of Marshall County. However, insufficient hydrogeochemical data are available for the Pennsylvanian bedrock in Marshall County.

Sr/Ca Molal Ratio.--The Sr/Ca molal ratio (Sr/Ca) was calculated to evaluate if any systematic relationships existed between hydrogeologic units and concentrations of Sr and Ca in the ground water. The chemistry of Sr is similar to that of Ca, and in Permian limestones of Kansas the Sr/Ca ranges from 2.5×10^{-3} to 5×10^{-3} (Chandhuri, pers. comm.). Strougstad and Horr (1963) reported Sr concentrations of up to 10 mg/L for low-salinity ground water in the U.S., although most values were less than 2 mg/L. The concentration of Sr in oil-field brines commonly exceeds 30 mg/L (White et al., 1963).

The Sr concentrations for ground water in the investigation area range from about 0.1 to 15 mg/L, although in most samples the concentration was less than 1.0 mg/L. All samples were undersaturated with respect to strontianite and celestite. The highest Sr concentrations are associated with high concentrations of Ca and SO_4, suggesting the dissolution of small amounts of celestite in the dissolving gypsum.

The Sr/Ca is variable and ranges from about 0.05×10^{-2} to 4.6×10^{-2}, although only 5 wells had a value exceeding 1.0×10^{-2}. The Sr/Ca values greater than 1.0×10^{-2} were in samples collected from the bedrock or glacial deposits, which contained elevated concentrations of dissolved SO_4. However, ground-water samples with elevated SO_4 concentrations do not always have high Sr/Ca. Thus, it appears that in some regions, gypsum contains small amounts of celestite which dissolves causing an increase in Sr/Ca.

Sass and Starinsky (1979) showed that the Sr/Ca can be an indicator of the chemical reactions occurring between aquifer minerals and solutions. They found there are six chemical processes which exert a control on Sr/Ca of a solution, including (1) dolomitization of calcite, (2) dolomitization of aragonite, (3) solution-reprecipitation of calcite, (4) transformation of aragonite to calcite, (5) equilibrium with coexisting strontianite-calcite, and (6) equilibrium with coexisting celestite-calcite. Because the ground water is significantly undersaturated with respect to strontianite and celestite, processes 5 and 6 are unlikely as a control on Sr/Ca.

The range of Sr/Ca for ground-water samples which do not appear to be affected by celestite dissolution is 0.05×10^{-2} to 1.0×10^{-2}. These values suggest that the ground water is interacting with aquifer minerals resulting in solution and reprecipitation of calcite (Sass and Starinsky, 1979, p. 892) This is supported by the SI_c data which show that many of the samples, especially those from bedrock and glacial deposits, are near saturation.

Na vs K.--The concentrations of Na and K in ground-water samples from the tills are probably appreciably influenced by cation-exchange reactions. The concentrations of Na and K for all samples are generally positively correlated

but have a great degree of scatter (Fig. 17). The highest concentrations and widest range of values for K are found in till-water samples. The relative molal concentrations of Na are greater than K by at least an order of magnitude.

The high values of Na and K in the ground water from the glacial deposits are probably the result of ion exchange reactions involving smectite clays, although a minor contribution of these ions is probable from the dissolution of feldspars or salts in the till (Paces, 1972, p. 222-223; Grisak et al., 1976, p. 323). The Na and K on the clays are probably being exchanged for Ca or Mg in the ground water. The relatively higher concentrations of Na over K in the ground water are probably a reflection of the greater abundance of exchangeable Na on the clays and the more tightly held K in the clay structure.

The lowest concentrations of K are found in ground-water samples from bedrock. Concentrations are always below 2 mg/L and are commonly below 1 mg/L. This low and relatively narrow range of K concentrations is likely a reflection of the low K content of the Ca-rich limestone aquifers. Also, the abundant illite of the bedrock shales, which contains K as an interlayer cation, is not likely to release much K. Regardless of the mechanism, it is apparent that aquifer mineralogy is a major factor controlling Na and K hydrochemistry.

Na vs Cl.--The concentrations of Na and Cl are generally positively correlated in samples from all hydrogeologic units, but with molal concentrations of Na greater than those of Cl (Fig. 18). Till-water samples have the highest concentrations and the widest range of concentration for both ions. Samples from the buried channel generally have the lowest concentrations.
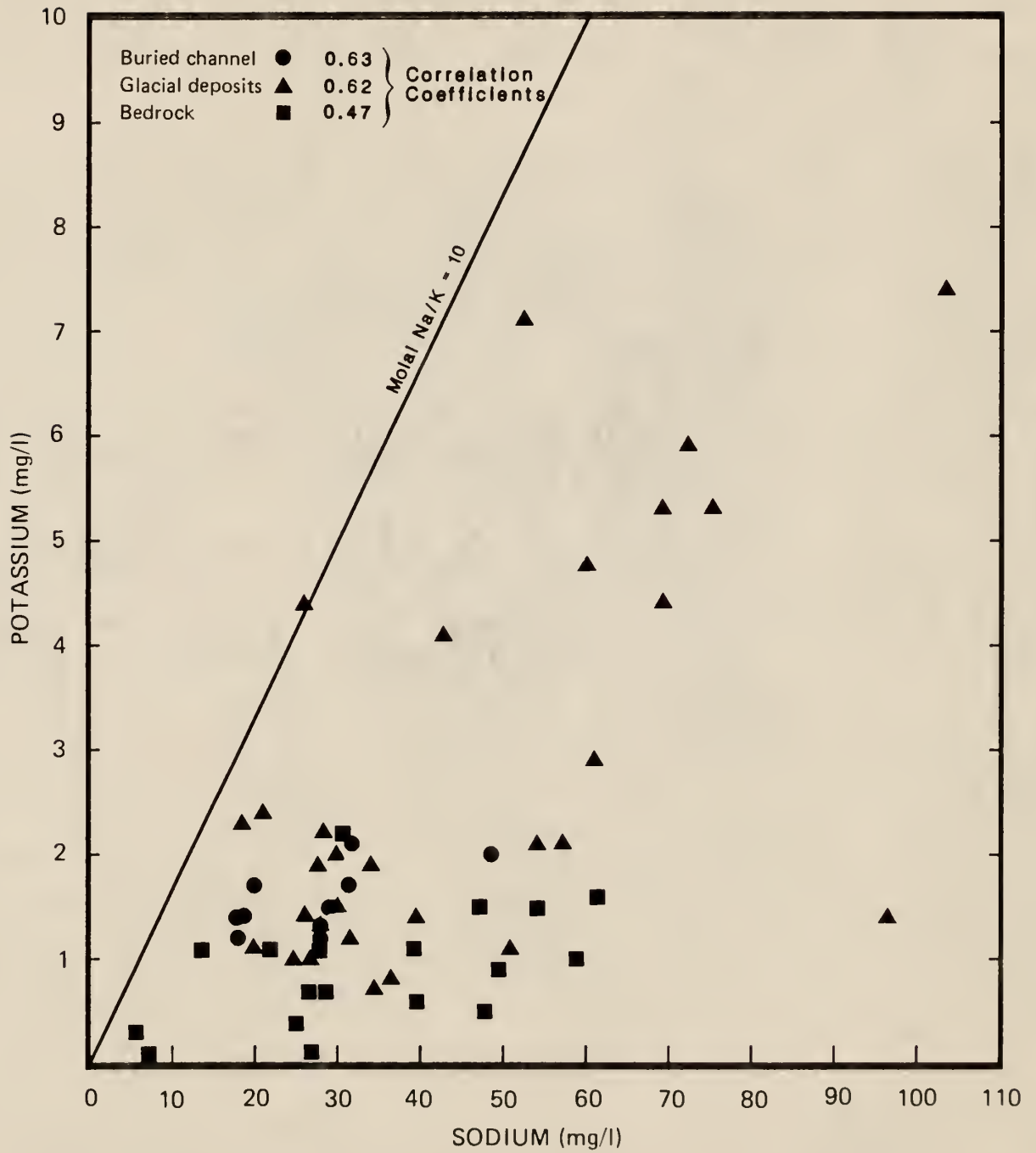
Figure 17 - **Scatter diagram of Na vs K**
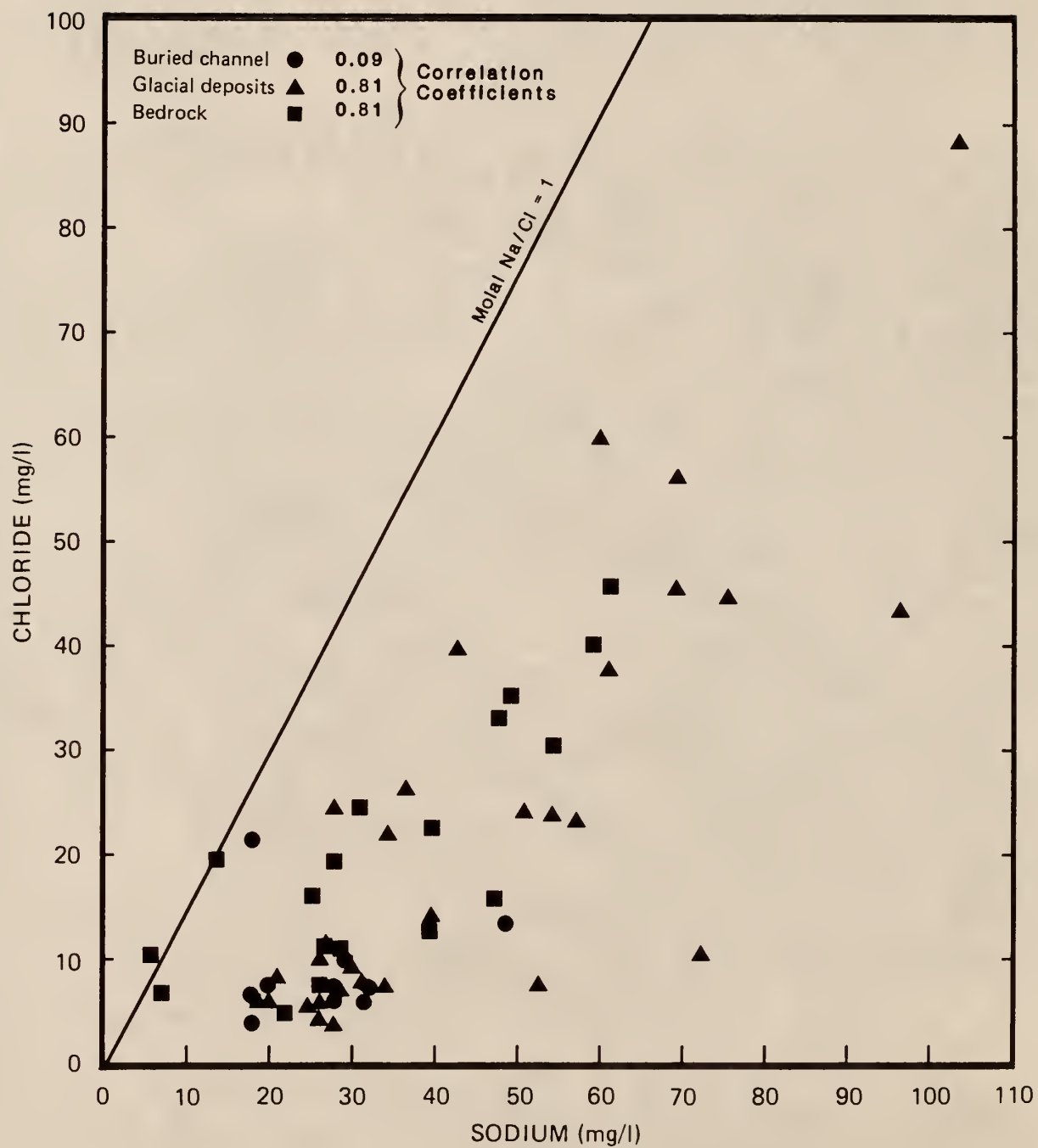
Figure 18 - **Scatter diagram of Na vs Cl**

The origin of much of the Na and Cl in the ground water is probably the dissolution of small amounts of halite contained in evaporite sequences in bedrock or glacial till (Grisak et al., 1976, p. 323; Whittemore et al., 1982, p. 31) and/or traces of Na and Cl trapped in the carbonate minerals and gypsum. The contribution of Na to the ground water from the dissolution of feldspars is probably much less than 10 mg/L (Grisak et al., 1976, p. 323). The positive correlation of Na and Cl suggests that either halite dissolution or Na and Cl originally present as trapped seawater in the carbonates and gypsum have the greatest impact on concentrations of these ions in solution. Concentration of salts in the tills by evapotranspiration could also have increased Na and Cl contents.

The greater molal content of Na over Cl indicates some geochemical process has resulted in a relative increase in Na or a decrease in Cl. The Cl ion is a conservative ion and generally is not removed from solution by chemical processes such as precipitation, ion exchange or oxidation-reduction reactions (Hem, 1970, p. 170-176). Chloride concentrations are generally only affected by physical processes such as dilution. The Na ion is also somewhat conservative, but commonly does enter into ion exchange reactions with clays. It is unlikely that precipitation is an important factor affecting the Na concentrations because Na does not enter into precipitation reactions at the concentration range of these waters. The excess dissolved Na is probably derived from ion exchange reactions.

The relative large degree of scatter in the Na data, particularly in samples from the glacial deposits, also implies that Na values have been altered by ion exchange involving the smectite clays. The effects of this exchange on concentrations of Ca and Mg are not readily discernible. The concentrations of Ca and Mg are generally much greater than Na. Thus, because

the exchange is on a milliequivalent basis, percentage changes in the Ca and Mg concentration are smaller than for Na.

Hydrochemical System

The hydrochemical evolution of ground water in all hydrogeologic units in the investigation area appears to be dominated by dissolution-precipitation of carbonate minerals such as calcite and dolomite (Eqs. 4 and 5) under open-system conditions (Eq. 7). The dissolution of carbonate minerals has a major impact on the hydrochemistry of ground water because they are ubiquitous in all hydrogeologic units and are relatively soluble. The ground water also reacts with other minerals by dissolution or ion exchange, but the impact of these reactions is limited to certain hydrogeologic units.

Ground water from the infiltration of surface water or precipitation becomes charged with CO_2 because of elevated P_{CO_2} in the soil zone. The CO_2 reacts with the ground water, generating H_2CO_3 and lowering pH. The ground water dissolves carbonate minerals in the rocks and continues this process during deep percolation until the ground water becomes saturated with calcite and in some cases dolomite. The solubilities of calcite and dolomite act to limit the maximum concentrations of Ca, Mg, and HCO_3, and upper limit of pH of the ground water. The open-system condition with respect to CO_2 replenishment is at least partly responsible for moderating ground-water pH.

The dissolution of gypsum has a major impact on the hydrochemistry of ground water in the bedrock. Ground water never reaches saturation with gypsum and it does not precipitate from solution. However, the incongruent dissolution of gypsum increases the concentration of Ca in the ground water, which results in precipitation of calcite from supersaturated waters. The relative kinetics of calcite precipitation and gypsum dissolution may be

responsible for the slight supersaturation with respect to calcite, and perhaps dolomite, in some waters.

The removal of Ca and HCO_3 from the ground water affects ion ratios in solution. The distinctly different Ca/Mg, Ca/HCO_3, and Ca/SO_4 in some waters (Figs. 13, 15, and 16) can be related to the incongruent solution reactions. The high concentrations of Ca and SO_4 in some of the ground waters also causes increased concentrations of some other ions because the higher ionic strength of the water decreases activity coefficients allowing increased equilibrium concentrations (Eqs. 2 and 3).

Ground water from the glacial deposits may be greatly affected by ion exchange reactions. The most noticeable effects are increases in the concentrations of Na and K in the ground water from ion exchange. The Na and K enter solution as Ca and Mg are adsorbed on the clays. These reactions also have an impact on ion ratios in the ground water (Figs. 17 and 18).

The consistent hydrochemistry of the buried channel is related to the relatively simple and homogeneous mineralogy of the aquifer materials and the nature of the source of ground-water recharge. The chert gravels are composed of principally chert and limestone fragments. Soluble minerals such as gypsum and halite were probably not deposited with these sediments. A small amount of variation may be imparted on these waters by the heterogeneity of the alluvium through which the ground water must pass before reaching the chert gravels. However, the alluvial deposits probably contain very little highly soluble minerals. The relatively large reservoir of water in the saturated alluvium of Robidoux Creek and Black Vermillion River could act to buffer any significant changes in hydrochemistry. Large changes in hydrochemistry of the alluvium would probably only occur during severe, prolonged drought conditions.

SUMMARY AND CONCLUSIONS

The buried channel in southeast Marshall County is a subtle depression in the bedrock surface that trends from northwest to southeast across the investigation area. The channel is asymmetrical in cross section, generally widening to the southeast. The widest and most subtle part of the channel is along the eastern edge of the investigation area, along the Marshall-Nemaha county line. The channel is over 6 miles wide at this location.

The bedrock surface along the main axis of the channel slopes to the southeast at 4 to 5 feet per mile. Tributaries to the channel are recognized in some areas. The bedrock surface beneath the alluvium of the Black Vermillion River southwest of Frankfort is probably the largest such tributary. This tributary once was part of a preglacial drainage system that flowed to the southeast across northeast Kansas. Another tributary may exist to the northeast of the channel's main axis, but drill hole data are sparse in that area.

The major aquifer of the buried channel is a 20-foot-thick deposit of chert gravel occurring at the base of the channel. Ground water in the chert gravels may be locally confined as indicated by water levels as much as 100 feet above the top of the gravels or may reflect the hydraulic connection between the gravels and overlying sands. Ground water flows to the southeast parallel to the bedrock-surface gradient. Flow in the Black Vermillion River tributary is probably to the northeast toward the axis of the channel.

The hydrochemical evolution of ground water in the investigation area is generally controlled by the aquifer's bulk mineralogy. Variations in the hydrochemistry can be related to mineralogical differences among hydrogeologic units. Because all aquifers contain abundant carbonate minerals such as

calcite and dolomite, the hydrochemical evolution of the ground water is dominated by dissolution-precipitation reactions involving these minerals. The elevated P_{CO_2} levels in all ground-water samples indicate open-system conditions with respect to CO_2 replenishment. Carbonate equilibria is responsible for the upper limits of Ca, Mg, HCO_3 concentrations, and buffers pH in all hydrogeologic units.

The presence of relatively soluble gypsum in the bedrock has a major impact on the hydrochemistry of those aquifers. A small amount of gypsum may also be present in the glacial deposits, but does not appear to have as dramatic an impact on hydrochemistry. Ion exchange reactions involving smectite clays in the glacial deposits and traces of Na and Cl trapped in carbonate minerals and gypsum result in increased concentrations of Na and K.

Ground water in the buried channel generally has the lowest TDS and shows the least geographic and temporal variation in hydrochemistry of any of the hydrogeologic units. Concentrations of the major ions do not appear to increase significantly over the length of the channel in Marshall County, although TDS, and particularly SO_4 concentrations, increase dramatically in the buried channel in Nemaha County.

Ground water recharge to the buried channel is probably occurring where chert gravels pass under the saturated alluvium of Robidoux Creek and Black Vermillion River. Geologic logs show that the alluvium is hydraulically connected to the chert gravels in some areas. Water levels in the gravels are similar to surface water elevations.

The hydrochemistry of the buried channel indicates that only a small amount of ground-water recharge originates from Permian bedrock. If a large proportion of the total recharge were being contributed by underflow from

Permian bedrock, the water quality of the buried channel would reflect such a contribution. The most likely indicator of such recharge would be increased SO_4 concentrations. The ground water in the buried channel is low in SO_4, in contrast with much higher SO_4 contents in Permian bedrock waters. Underflow from the Pennsylvanian bedrock could be contributing a significant amount of recharge to the buried channel along the east side of Marshall County. However, insufficient hydrochemical and hydrogeologic data are available to determine this component of recharge. The glacial deposits are probably contributing to recharge to some extent, but the relatively low permeability of these deposits suggests only a small quantity of recharge is occurring.

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Appendix A

ANALYTICAL PROCEDURES

HYDROGEN ION ACTIVITY

Method: Potentiometric measurement

Apparatus: Corning Model 610 portable pH meter with Thomas combination electrode and pH 4, 7, and 8 buffers.

Procedure: 1.) Check battery condition by turning function knob to 'BATT CK'. Replace batteries if needle falls outside green band.

2.) Turn function knob to 'pH Normal' and set temperature knob to temperature of buffers and sample.

3.) Rinse electrode with distilled-deionized (D-D) water and blot dry. Lower into pH 7 buffer. Adjust calibrate knob to read pH of buffer.

4.) Rinse and dry electrode. Lower into pH 4 buffer and adjust temperature knob to obtain correct reading.

5.) Recheck calibration with pH 8 buffer.

6.) Rinse and dry electrode. Lower into sample and read pH.

Note: Turn function knob to 'OFF' position when electrode is not immersed.

SPECIFIC ELECTRICAL CONDUCTIVITY

Method: Specific Conductivity Electrode and Meter

Apparatus: Lab-Line Lectro Mho-Meter, Model MC-1, Mark IV conductivity meter, Lab-Line epoxy conductivity cell with cell constant of 1.032 (Whittemore, pers. comm.), thermometer graduated in 0.1°C.

Procedure: 1.) Set selector switch to 1000 and temperature dial to 25°C.

2.) Measure and record temperature of sample to nearest 0.1°C.

3.) Rinse conductivity cell in sample, then completely immerse the black porcelain tip of the cell in the sample. Swirl the cell to remove trapped air bubbles.

4.) Press the READ button and record conductivity in micromhos/cm.

5.) Correct conductivity reading to 25°C using the following relationship:

SEC at 25°C = (measured conductivity)(1.032)(1+0.02(25-sample temp.))

METALS DETERMINATIONS

Method: Spectrophotometric procedures used in analysis of the metals
            calcium, magnesium, strontium, sodium, and potassium are
            similar and are discussed together. Calcium, magnesium, and
            strontium were analyzed by atomic absorption. Sodium and
            potassium were analyzed by flame emission.

Apparatus: Perkin-Elmer 305B atomic absorption/flame emission
            spectrophotometer, lamps for calcium, magnesium, and
            strontium, 1000 mg/L calcium stock, 1000 mg/L magnesium
            stock, 100 mg/L strontium stock, 1000 mg/L sodium stock,
            100 mg/L potassium stock, and a solution containing 10000
            mg/L lanthanum and 2000 mg/L rubidium.

Procedure: 1.) Prepare 1000 mg/L calcium stock by dissolving 2.4971 g
                 reagent grade $CaCO_3$, previously dried at 110°C for
                 two hours, in 200 mL D-D water. Add 10-20 mL HCl until
                 $CaCO_3$ completely dissolves. Dilute to one liter with
                 D-D water.

            2.) Prepare 1000 mg/L magnesium stock by dissolving
                 10.134 g reagent grade $MgSO_4 \cdot 7H_2O$ in 200 mL D-D
                 water. Dilute to one liter with D-D water.

            3.) Prepare 100 mg/L strontium stock by dissolving 0.1686 g
                 reagent grade $SrCO_3$, previously dried at 200°C for
                 2 hours, in 200 mL D-D water. Add 10-20 mL HCl until
                 $SrCO_3$ completely dissolves. Dilute to one liter with
                 D-D water.

            4.) Prepare 1000 mg/L sodium stock by dissolving 2.305 g
                 reagent grade Na_2CO_3, previously dried at 110°C for
                 two hours, in 200 mL D-D water. Dilute to one liter
                 with D-D water.

            5.) Prepare 100 mg/L potassium stock by dissolving 0.1907 g
                 reagent grade KCl, previously dried at 110°C for 1
                 hour, in 200 mL with D-D water. Dilute to one liter
                 with D-D water.

            6.) Prepare lanthanum-rubidium solution by dissolving
                 25.4 g primary grade $LaCl_3 \cdot 6H_2O$ and 2.8269 g
                 reagent grade RbCl in 500 mL D-D water. Dilute to 1000
                 mL with D-D water.

            7.) Prepare metals standards by adding appropriate volumes
                 of each stock solution to 500 mL of lanthanum-rubidium
                 solution followed by dilution to 1000 mL with D-D
                 water. The range of concentration covered by the
                 standards for each metal depends on the linear range of
                 that element for the particular instrument
                 configuration. For this investigation, instrument
                 settings were those recommended by Perkin-Elmer. The
                 following standards were used (in mg/L):

Ion	A	B	C	D
Ca	5.00	3.00	1.00	0.50
Mg	0.50	0.30	0.10	
Sr	2.00	1.00	0.50	
Na	1.00	0.50	0.10	
K	2.00	1.00	0.50	

8.) Samples must be sufficiently diluted to bring the concentration of each metal into the linear range of that element for the particular instrument setting.

BICARBONATE DETERMINATION, HCO_3

Method: Titration (Modified from Skougstad et al., 1979)

Apparatus: Corning Model 12 pH meter, 25 mL buret, magnetic stirrer, and thermometer graduated in 0.1°C.

Procedure:
1.) Prepare approximately 0.009 M Na_2CO_3 by dissolving 0.9531 g Na_2CO_3, previously dried at 150°C for two hours, in 500 mL D-D water. Dilute solution to 1 liter.

2.) Prepare 0.018 N H_2SO_4 by diluting to one liter with D-D water, 0.5 mL concentrated H_2SO_4.

3.) Standardize acid by titrating to the end point of Na_2CO_3 solution.

4.) Calculate normality of acid according to the formula:

$$N\ H_2SO_4 = 2(mL\ Na_2CO_3\ solution)(M\ Na_2CO_3)/(mL\ H_2SO_4\ titrated)$$

5.) Pipette 50 mL of sample into plastic beaker containing a Teflon stirring bar.

6.) Fill 25 mL buret with H_2SO_4 and record initial reading on buret.

7.) Calibrate pH meter. Position beaker in center of stirrer surface. Turn on stirrer to lowest possible setting. If necessary, reposition beaker for smooth stirring. Lower electrode into beaker and wait for meter reading to stabilize. Measure and record temperature and pH of sample.

8.) Titrate H_2SO_4 until pH of sample reads 4.5. Three successive titrations should be reproducible to within 1 percent.

9.) Calculate concentration of HCO_3:

$$mg/L\ HCO_3 = (61.02)(1000)(mL\ H_2SO_4\ titrated)(N\ H_2SO_4)/(mL\ sample)$$

Note: Bicarbonate is not stable and caution must be taken to avoid outgassing of sample. Keep sample chilled at 4°C at all times prior to HCO_3 determination. Bicarbonate analysis should be conducted within 24 hours of sample collection.

CHLORIDE DETERMINATION, Cl

Method: Mohr titration (Modified from American Public Health Association et al., 1975, technique 407A).

Apparatus: 25 mL buret, 100 mL beaker, magnetic stirrer, 1000 mg/L chloride stock solution, potassium chromate indicator, silver nitrate stock solution, incandescent lamp with yellow bulb.

Procedure: 1.) Prepare 1000 mg/L chloride stock solution by dissolving in D-D water 1.6491 g NaCl, previously dried for one hour at 110°C. Dilute to one liter with D-D water.

2.) Prepare 100 mg/L and 10 mg/L chloride standard solutions by diluting to one liter, 100 mL, and 10 mL of stock solution, respectively.

3.) Prepare silver nitrate standard titrant solution (approximately 760 mg/L silver) by dissolving in D-D water 1.1978 g $AgNO_3$, previously dried for 40 minutes at 100°C. Dilute to one liter with D-D water. Standardize against 100 mg/L chloride standard solution.

4.) Prepare potassium chromate indicator solution by dissolving 25 g K_2CrO_4 in D-D water. Dilute to one liter with D-D water.

5.) Pipette 20 to 50 mL of sample into beaker. Add a few drops indicator solution. Fill buret with standardized silver nitrate solution and record initial buret reading. Begin to slowly add the silver nitrate solution to the sample. Because the color of the solution turns red when the end point is reached, the best titration results were obtained in a darkened room with only the yellow bulb shining directly on the sample being analyzed.

6.) Continue titration until the red-colored silver chromate persists in the sample. Be careful not to pass end point and to be consistent in the end point recognition. It is recommended that many practice titrations be conducted on known chloride standards to help in end point recognition.

7.) Calculations:

$$\text{mg/L Cl} = (\text{mL } AgNO_3 \text{ titrated})(\text{N } AgNO_3)(35,453)/(\text{mL sample})$$

SULFATE DETERMINATION, SO_4

Method: Turbidimetric (Modified from American Public Health
            Association et al., 1975, technique 426C)

Apparatus: Coleman Universal Spectrophotometer, magnetic stirrer,
            500 mg/L sulfate stock solution, 30-40 mesh $BaCl_2$
            crystals, salt-acid glycerol solution.

Procedure: 1.) Prepare 500 mg/L SO_4 stock solution by dissolving in
                 D-D water 0.7393 g Na_2SO_4, dried at 105°C for 2
                 hours, and diluting to 1 liter of solution. From this
                 stock solution prepare standards of 5, 10, 15, 20, 25,
                 and 30 mg/L.

            2.) Prepare salt acid glycerol solution by dissolving 75 g
                 NaCl in about 300 mL distilled deionized water. Add
                 30 mL concentrated HCl and 100 mL 95 percent ethyl
                 alcohol. Mix this solution with 50 mL glycerol.

            3.) Pipette 50 mL of standard or sample into a 100 mL
                 beaker and add 10 mL of salt-acid glycerol solution.
                 Put in magnetic stirrer and begin slowly stirring. Add
                 about 0.3 g of 30-40 mesh $BaCl_2$ crystals and continue
                 stirring for about 1 minute.

            4.) Stop stirrer for 3.5 minutes and then stir again for
                 0.5 minute.

            5.) Pour sample into a 19 x 105 mm Coleman cuvette making
                 sure cuvette is absolutely clean and is in the same
                 orientation for all analyses.

            6.) Within 5 minutes of final stirring, read the percent
                 transmittance on the spectrophotometer by comparing
                 each aliquot against a blank solution containing 50 mL
                 of sample and 10 mL salt acid-glycerol solution. Do
                 not add $BaCl_2$ crystals to blank. Analyze samples
                 according to the Null Method (Coleman instruction
                 manual).

            7.) Calculations: On semi-log paper plot a standard curve
                 with the sulfate concentration in mg/L on the
                 arithmetic abscissa and percent transmittance on the
                 logarithmetric ordinate. Sulfate concentrations in
                 samples are read in mg/L from the standard curve.
                 Correct for any sample dilution.

Notes on spectrophotometer use: Allow spectrophotometer to warm up at least
one-half hour before its use. Drifting readings are an indication that the
unit is not sufficiently warmed up. Cuvettes used in the sulfate
determination must be a matched pair. Cuvettes must not be handled with
bare fingers. Use appropriate gloves or Kim Wipes when handling cuvettes.
If cuvettes are touched with fingers, wipe clean immediately with Kim

Wipes. After each use cuvettes must be thoroughly cleaned with a brush to prevent the buildup of residue, and then should be placed back in storage box.

NITRATE DETERMINATION, NO_3

Method: Spectrophotometric absorption (Modified from American Public Health Association et al., 1975)

Apparatus: Perkin-Elmer Spectrophotometer for operation at 220 and 275 nm, matched silica cells of 1 cm or longer light path, 200 mg/L nitrate stock solution, HCl.

Procedure: 1.) Prepare a 200.0 mg/L NO_3 stock solution by dissolving 0.3261 g KNO_3, previously dried at 100°C for one hour, in 500 mL D-D water. Dilute solution to 1 liter.

2.) Prepare standard NO_3 solutions of 1, 3, 5, 10, and 15 mg/L NO_3 by diluting appropriate volumes of stock solution to 200 mL. Treat standards in the same manner as samples. Acidify standards to pH 3 with HCl prior to final dilution.

3.) Turn on spectrophotometer and allow to warm up for 15 minutes. Set wavelength at 220 nm. Zero spectrophotometer according to manufacturer's instructions.

4.) Construct calibration curve for standards by comparing absorbance of acidified D-D water blank to absorbance of each standard. Plot absorbance vs NO_3 concentration in mg/L on semi-log paper.

5.) Read absorbance of samples against acidified D-D water blank.

6.) Set wavelength at 275 nm. Zero spectrophotometer according to manufacturer's instructions.

7.) Repeat step 5 for all samples at new wavelength. This step corrects for presence of dissolved organic matter.

8.) Calculations: NO_3 absorbance = (absorbance at 220 nm)-(2(Absorbance at 275 nm))

9.) Plot NO_3 absorbance on calibration curve and read corresponding concentration in mg/L. Correct for any dilutions.

Appendix B

GEOLOGIC LOGS OF TEST BORINGS

<u>3-8-9ada</u>

Well log of a test hole approximately 200 feet north of the railroad tracks on
Home City road at the northeast corner of the southeast one-quarter of the
northeast one-quarter of sec. 9, T.3S., R.8E., (3-8-9ada), on the east side of
the road, drilled on June 8, 1982. Surface elevation: 1298 feet above MSL
(Mean Sea Level)

	Thickness, feet	Depth, feet
Quaternary - Pleistocene		
Silty clay, reddish	12	0- 12
Clayey sand, reddish	18	12- 30
Silty clay, reddish brown	15	30- 45
Clayey silt, brown	1	45- 46
Sand, brown, with reddish coarse sand-sized sandstone fragments and other sand-sized grains	9	46- 55
Clay, dark gray	48	55-103
Gravel, chert (?)	2	103-105
Permian		
Shale, blue-green	7	105-112
Shale, red-brown	>1	112-113
	Total depth	113

3-8-20ccc

Well log of a test hole 600 feet east of extreme southwest corner of sec. 20,
T.3S., R.8E., (3-8-20ccc), on the north side of the road, drilled on June 3,
1982. Surface elevation: 1320 feet above MSL

	Thickness, feet	Depth, feet
Quaternary - Pleistocene		
Clay, reddish, with minor amounts of coarse sand	26	0- 26
Till, reddish, silty	20	26- 46
Hard layer, unknown lithology	1	46- 47
Sand, fine, loose, with sand-sized chert at 70-foot interval	58	47-105
Sand, coarse, with minor amount of chert	13	105-118
Sand, very coarse to fine gravel, contains blue chert, quartz and quartzite fragments	4	118-122
Sand, fine	18	122-140
Sand, coarse, cherty	30	140-170
Sand, coarse to very coarse	21	170-191
Clay, white	5	191-196
Clay, hard, with some white and dark gray clay, with sand-sized chert	2	196-198
Permian		
Shale, black	>1	199
	Total depth	199

3-8-21aaa

Well log of a test hole 150 feet west of extreme northeast corner of sec. 21,
T.3S., R.8E., (3-8-21aaa), on the south shoulder of the road, drilled on June
7, 1982. Surface elevation: 1275 feet above MSL

	Thickness, feet	Depth, feet
Quaternary - Pleistocene		
Road fill	2	0- 2
Clay, reddish, sandy, with sand-sized chert between 8 and 9 feet	7	2- 9
Clay, reddish to brown, cherty	20	9- 29
Silty clay, dark gray	30	29- 59
Sand, gray, loose, with minor amounts of reddish sand	115	59-174
Permian (?)		
Shale, black	?	174
	Total depth	174

4-10-17ccc

Well log of a test hole 25 feet east of southwest corner of sec. 17, T.4S.,
R.10E., (4-10-17ccc), on the east side of the road, drilled on March 17,
1982. Surface elevation: 1214 feet above MSL

	Thickness, feet	Depth, feet
Quaternary - Pleistocene		
Clay, black, topsoil	13	0-13
Silty clay, dark gray	17	13-30
Sand, dark olive gray	9	30-39
Sand, slightly coarser than above	11	39-50
Clayey sand, gray	16	50-71
Permian (?)		
Shale, red	>5	76
	Total depth	76

4-10-19ddd

Well log of a test hole 100 feet west of southeast corner of sec. 19, T.4S.,
R.10E., (4-10-19ddd), in the middle of the road, drilled on March 17, 1982.
Surface elevation: 1256 feet above MSL

	Thickness, feet	Depth, feet
Quaternary - Pleistocene		
Topsoil, black	6	0- 6
Silty clay, reddish to dark brown	5	6-11
Silty clay, light brown, minor amount of fine pebbles of limestone	5	11-16
Silty clay, light brown, minor amount of fine pebbles of chert, iron-stained sandstone, and limestone	5	16-21
Sand, clean, dry, quartz	6	21-27
Sand, with minor clay lenses	4	27-31
Sand	2	31-33
Permian (?)		
Limestone, very hard	?	33
	Total depth	33

4-10-28ccc

Well log of a test hole 50 feet east of southwest corner of sec. 28, T.4S.,
R.10.E, (4-10-28ccc), on the north side of the road, drilled on March 16,
1982. Surface elevation: 1294 feet above MSL

	Thickness, feet	Depth, feet
Quaternary - Pleistocene		
Topsoil	1	0- 1
Silty to sandy clay, light brown	25	1- 26
Sandy clay, gray-green, fine pebbles	10	26- 36
Sandy clay, dark brown to blue-gray fine pebbles	5	36- 41
Sandy clay, dark gray	30	41- 71
Clayey sand, gray-green, sand is mostly quartz	5	71- 76
Sand, dark gray, mostly quartz	30	76-106
Permian (?)		
Shale, light orange and dark gray, hard, dry	>15	121
	Total depth	121

5-10-1ccc

Well log of a test hole at the extreme southwest corner of sec. 1, T.5S., R.10E., (5-10-1ccc), on the north side of the road, drilled on March 17, 1982. Surface elevation: 1362 feet above MSL

	Thickness, feet	Depth, feet
Quaternary - Pleistocene		
Topsoil	3	0 - 3
Gravelly clay, yellow	15	3 - 18
Clay, gray-tan, pebbley	29	18 - 47
Clayey gravel, hard at 64.5-66.5	19.5	47 - 66.5
Sandy clay, medium dark gray	10.5	66.5- 77
Gravelly to sandy clay, medium gray	14	77 - 91
Sand, tan, very fine, some gravel	81	91 -172
Clay, gray	47	172 -219
Permian (?)		
Limestone, hard	2	221
Shale, hard	2	223
Limestone	?	223
	Total depth	223

5-10-3ccc

Well log of a test hole 75 feet east of southwest corner of sec. 3, T.5S., R.10E., (5-10-3ccc) on the north side of the road, drilled on March 15, 1982. Surface elevation: 1259 feet above MSL

	Thickness, feet	Depth, feet
Quaternary - Pleistocene		
Topsoil, dark brown	2	0- 2
Silty clay, dark gray	8	2-10
Silty clay, brown	12	10-22
Silty clay, blue-gray	5	22-27
Clay, blue, small amounts green clay	5	27-32
Sandy clay, green, minor amount coarse sand of chert and limestone	1	32-33
Permian (?)		
Shale, light green	14	33-47
Shale, red	>13	47-60
	Total depth	60

Appendix C

RESULTS OF ANALYSES OF GROUND-WATER SAMPLES

Table C1. Locations of Wells From Which Ground-Water Samples Were Collected

Name	Sample Location[1]
A. Maas	4-9-1dcd
L. Gerstner	4-9-1cdc
J. Dunlap	4-9-11bbc
J. Stiner	4-9-17abb
J. Horigan	4-9-3ddc
C. Swick	4-10-9baa
H. Huddleston	4-10-3cc
M. Bramhall	5-10-14ada
G. Feldhausen	3-9-33dcd
J. Sanderson	3-8-19dad
L. Baker	5-10-23bcb
D. Schooler	4-9-9bda
K. Lindsey	3-9-33ddd
W. Foley	3-8-29ddd
B. Bramhall	4-10-10cdd
W. Hanzlik	4-10-23acc
L. Wenzl	4-10-27aaa
J. Boyle	3-10-36bcc
C. Seematter	3-8-24bdb
D. Stock	3-8-4dcd
L. Ladner	3-9-12ddd
H. Wullschleger	3-8-3daa
B. Bliss	5-10-2dcc
D. Fincham	3-8-30aaa
C. Stiner	4-10-5bba
L. Millenbruch	3-8-15bbc
J. Vogelsburg	3-8-14bba
E. Foley	3-8-14ada
G. Norman	3-8-16ccc
L. Ketter	3-8-22daa
A. Argo	3-10-20cdc
B. Alley	5-9-19bcd
E. Ewing	5-8-36daa
V. Forst	5-9-32add
D. Bonjour	6-10-4aba
H. Haskin	5-9-4bab
W. Surdez	5-10-7ada
R. Koch	5-9-14bbb
J. Wapp	5-9-21caa
D. Fincham	4-8-20d
M. Samuelson	3-9-4aba
L. Boeckman	5-10-19cca

* Township-Range-Section, 1/4 Section, 1/4-1/4 Section, 1/4-1/4-1/4 Section

Table C2. Results of Analyses of Ground-Water Samples from the Buried Channel

Name	Sample Date	Ca	Mg	Sr	Na	K	HCO$_3$	Cl	SO$_4$	NO$_3$	pH	T, °C	SEC	Charge Balance Error %
A. Maas	9/25/82	90.	11.	0.2	18.	1.4	320	21.	6.0	5.4	7.02	14.3	590	0.7
A. Maas	1/13/83	85.	11.	0.4	20.	1.7	340	7.5	13.	0.3	7.04	12.8	550	-0.8
A. Maas	6/ 8/83	86.	9.9	0.3	18.	1.4	350	6.3	11.	0.4	7.05	14.4	570	-1.2
A. Maas	9/ 9/83	90.	11.	0.4	18.	1.2	340	3.8	12.	0.4	7.08	14.7	610	1.8
L. Gerstner	1/13/83	97.	14.	0.5	29.	1.5	410	10.	26.	0.1	7.09	13.0	670	-1.4
L. Gerstner	6/ 8/83	100.	13.	0.4	28.	1.3	410	7.3	25.	0.1	6.98	13.9	690	-0.4
L. Gerstner	9/ 9/83	105.	14.	0.5	28.	1.2	410	6.1	24.	0.2	7.10	15.4	710	1.4
J. Dunlap	6/ 8/83	99.	21.	0.7	49.	2.0	450	13.	54.	4.4	7.02	14.5	810	-0.5
J. Stiner	6/11/83	87.	14.	0.5	32.	2.1	390	7.4	12.	0.1	7.08	14.7	630	0.3
J. Stiner	9/ 9/83	91.	14.	0.6	31.	1.7	390	5.8	15.	0.2	7.08	14.8	650	2.0

Notes: Concentrations expressed in mg/L.
SEC in micromho/cm at 25°C.

Table C3. Results of Analyses of Ground-Water Samples from Glacial Deposits

Name	Sample Date	Ca	Mg	Sr	Na	K	HCO₃	Cl	SO₄	NO₃	pH	T,°C	SEC	Charge Balance Error %
J. Horigan[+]	9/25/82	77.	12.	0.3	33.	1.4	380	14.	55.	0.1	7.14	14.2	740	-11.0
J. Horigan	1/13/83	102.	22.	0.6	54.	2.1	420	24.	95.	0.8	7.16	12.5	840	-1.3
J. Horigan	6/ 8/83	108.	21.	0.6	57.	2.1	420	23.	70.	0.1	7.10	13.8	860	3.0
C. Swick[+]	9/25/82	42.	4.4	0.3	19.	0.9	270	11.	8.0	40.	6.80	13.9	510	-24.6
C. Swick[+]	1/13/83	70.	9.2	0.6	16.	1.4	270	21.	19.	37.	6.82	13.4	570	-8.5
H. Huddleston	9/25/82	103.	14.	0.4	19.	2.3	400	6.1	16.	0.1	7.08	14.2	710	1.3
H. Huddleston	6/ 8/83	105.	16.	0.4	21.	2.4	420	8.2	19.	0.1	7.01	14.4	700	0.2
M. Bramhall	10/ 3/82	59.	16.	0.7	69.	5.3	350	45.	9.8	2.6	7.04	14.8	730	1.0
M. Bramhall	6/23/83	55.	16.	0.8	75.	5.3	360	45.	17.	0.3	7.25	15.2	750	-0.7
G. Feldhausen	2/19/83	52.	6.8	0.2	20.	1.1	230	5.7	4.0	1.3	7.18	13.4	390	<0.1
G. Feldhausen	6/23/83	52.	7.3	0.1	25.	1.0	230	5.3	4.2	2.5	7.20	14.2	420	2.5
J. Sanderson	2/19/83	77.	32.	0.9	40.	1.4	360	14.	74.	1.2	7.10	13.0	730	2.7
J. Sanderson	6/ 8/83	80.	33.	0.9	30.	1.5	360	9.4	78.	1.4	6.92	14.5	730	1.3
L. Baker	6/23/83	205.	47.	2.1	60.	4.8	480	60.	330.	0.3	7.20	14.2	1400	1.1
D. Schooler	6/23/83	61.	7.5	0.4	32.	1.2	260	7.5	31.	1.0	7.22	16.0	430	<0.1
K. Lindsey	6/23/83	84.	9.2	0.2	26.	1.4	320	5.6	29.	1.5	7.14	14.2	530	0.1
W. Foley	6/23/83	93.	28.	1.4	51.	1.1	420	24.	49.	26.	7.13	14.1	840	1.8
B. Bramhall	6/25/83	64.	9.2	0.3	28.	1.9	310	3.6	16.	0.1	7.31	15.0	530	-2.2
W. Hanzlik	6/25/83	112.	22.	0.6	26.	4.4	460	4.3	38.	0.1	7.19	16.0	770	1.6
L. Wenzl	6/25/83	58.	18.	0.6	104.	7.4	350	88.	31.	0.7	7.36	16.2	890	1.6

Table C3 (continued)

Name	Sample Date	Ca	Mg	Sr	Na	K	HCO₃	Cl	SO₄	NO₃	pH	T,°C	SEC	Charge Balance Error %
J. Boyle	6/25/83	94.	27.	0.7	53.	7.1	480	7.4	47.	1.0	7.22	15.8	820	1.6
C. Seematter	6/25/83	92.	19.	0.9	27.	1.0	350	11.	53.	1.6	7.19	14.0	660	1.8
D. Stock	6/30/83	84.	41.	2.0	30.	2.0	410	9.3	98.	1.5	7.30	15.1	810	-0.4
L. Ladner	6/30/83	92.	28.	6.4	72.	5.9	460	10.	107.	0.2	7.22	14.1	890	1.0
H. Wullschleger	6/30/83	90.	29.	1.0	36.	0.8	410	26.	55.	17.	7.05	14.2	850	-2.1
B. Bliss	6/ 8/83	50.	14.	0.7	61.	2.9	320	38.	18.	3.3	7.35	14.2	650	-2.0
D. Fincham	6/ 8/83	89.	30.	1.5	26.	1.4	380	9.9	77.	11.	7.07	13.8	730	-1.2
C. Stiner	6/11/83	84.	25.	1.0	43.	4.1	360	40.	32.	0.1	7.27	15.2	600	3.3
L. Millenbruch	6/30/83	133.	40.	2.7	69.	4.4	360	56.	240.	0.1	7.29	15.0	1200	1.8
J. Vogelsburg	6/30/83	111.	26.	0.7	28.	1.3	380	24.	44.	98.	7.09	13.8	1000	-3.0
E. Foley	7/ 5/83	73.	27.	1.0	34.	1.9	350	7.3	74.	0.3	7.13	14.0	690	-0.1
G. Norman	7/ 5/83	75.	22.	0.7	28.	2.2	360	6.8	20.	0.1	7.04	14.0	620	2.1
L. Ketter	7/ 5/83	96.	20.	0.4	34.	0.7	380	22.	57.	21.	7.03	14.8	760	-2.6
A. Argo	7/ 5/83	137.	28.	0.4	96.	1.4	390	43.	190.	125.	6.86	14.0	1300	-0.9

Notes: Concentrations expressed in mg/L.
SEC in micromho/cm at 25°C.
+ Charge balance error greater than 5 percent.

Table C4. Results of Analyses of Ground-Water Samples from Bedrock

Name	Sample Date	Ca	Mg	Sr	Na	K	HCO$_3$	Cl	SO$_4$	NO$_3$	pH	T,°C	SEC	Charge Balance Error %
B. Alley	7/18/82	105.	29.	1.3	28.	1.1	350	19.	120.	24.	7.25	14.0	940	-1.2
B. Alley	1/13/83	101.	28.	1.6	29.	0.7	370	11.	105.	18.	7.20	13.8	820	-1.2
B. Alley	6/11/83	100.	24.	1.2	27.	0.1	370	11.	63.	30.	7.18	13.7	810	-0.3
E. Ewing	7/18/82	200.	54.	1.0	61.	1.6	360	46.	420.	56.	7.12	13.0	1650	0.9
E. Ewing	1/13/83	176.	45.	1.3	54.	1.5	350	31.	340.	51.	6.97	12.8	1550	1.0
E. Ewing	6/11/83	195.	58.	1.9	59.	1.0	370	40.	410.	61.	6.95	13.0	1600	0.9
E. Ewing	9/ 9/83	156.	43.	1.4	40.	0.6	350	23.	280.	62.	7.15	13.4	1200	-0.7
V. Forst	7/18/82	280.	44.	0.6	14.	1.1	380	20.	500.	20.	6.97	13.0	1600	1.7
V. Forst	6/11/83	105.	18.	0.3	5.7	0.3	370	10.	17.	9.0	7.02	11.9	630	1.2
V. Forst	9/ 9/83	108.	18.	0.5	7.1	0.1	350	6.7	42.	1.3	7.02	12.1	620	2.6
D. Bonjour	6/23/83	142.	39.	0.1	48.	0.5	470	33.	121.	69.	6.92	12.8	1050	0.6
H. Haskin	6/25/83	97.	19.	0.7	26.	0.7	380	7.5	35.	14.	7.03	16.0	660	0.9
W. Surdez	6/30/83	158.	29.	4.5	22.	1.1	590	4.7	86.	0.1	6.98	17.0	1050	-1.6
R. Koch	6/11/83	104.	20.	0.9	25.	0.4	390	16.	60.	12.	7.08	14.2	670	-2.3
J. Wapp	6/11/83	270.	56.	8.1	39.	1.1	370	13.	630.	12.	6.97	13.0	1700	0.4
D. Fincham*	7/ 5/83	134.	23.	1.2	31.	2.2	410	25.	86.	41.	6.83	12.7	920	0.9
M. Samuelson	6/30/83	151.	50.	15.	47.	1.5	420	16.	250.	65.	7.19	13.8	1250	1.9
L. Boeckman	7/ 5/83	94.	35.	0.6	49.	0.9	400	35.	44.	83.	7.03	14.5	920	0.1

Notes: Concentrations expressed in mg/L.
SEC in micromho/cm at 25°C.
* Located outside investigation area

Appendix D

HISTORICAL HYDROCHEMICAL DATA

Appendix D. Historical Hydrochemical Data for Wells in the Investigation Area

Name	Sample Date	Ca	Mg	Na	K	HCO$_3$	Cl	SO$_4$	NO$_3$	pH	T,°C	SEC	Source	Aquifer
L. Hunninghake (5-10-6ddd)	6/ 5/81	116	25	13	1.8	339	4	117	0.1	7.7	13.6	748	KDHE	A
RWD 3 (3-8-32a)	3/ /76	83	11	21		332	8	10	1.0				Schwab-Eaton (1976)	D
	4/ /83	70	9.5	20	1.8	312	12	5.7	0.6	8.6			RWD3	D
	11/ /83	76	10.6	23	2.0	297	6.4	40	0.6	7.5		462	RWD3	D
	11/ /84					302	11	10	0.6			483	RWD3	D
Van Dorn (3-10-28cbc)	6/ 6/81	87	22	30	4.3	399	8	25	0.1	7.8	13.8	690	KDHE	C
A. Maas (4-9-1ddd)	6/ 6/81	88	11	19	1.9	337	5	14	0.1	7.6	14.0	541	KDHE	D
J. Stiner (4-10-17ba)	6/ 5/81	90	14	30	2.6	380	10	16	0.1	8.0	15.7	270	KDHE	D
M. Bramhall (5-10-14ada)	6/ 5/81	60	15	69	6.1	349	28	16	0.1	7.3	14.8	696	KDHE	C
V. Hunninghake (4-10-32bbb)	6/ 5/81	72	27	66	2.2	464	10	32	0.4	6.8	13.6	759	KDHE	C
H. Wullschleger (3-9-30cb)	6/ 6/81	80	9.5	21	1.9	279	6	24	4.7	7.6	13.7	553	KDHE	A
Unknown (3-8-36cd)	12/12/51	92	30	107*		427	12	205	4.9		12.8		Walters (1954)	B
Unknown (3-9-9bc)	12/12/51	208	54	63*		321	27	551	2.4		12.2		Walters (1954)	B
Unknown (4-8-3cd)	12/12/51	346	166	66*		249	18	1400	0.7		12.2		Walters (1954)	B
Frankfort Golf Course (4-9-16aac2)	3/22/50	78	15	27*		321	12	30	3.6	7.4			Walters (1954)	B
	10/12/64	78	15	28	2.2	317	15	30	1.2	7.3		560	KGS	B
	3/30/66	77	16	26	2.5	317	15	27	2.7	7.8		550	KGS	B
	3/22/67	79	15	28	2.5	315	15	35	2.7	7.6		570	KGS	B
	4/12/68	77	12	29	2.7	315	15	33	1.5	7.5		560	KGS	B

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Appendix D (continued)

Name	Sample Date	Ca	Mg	Na	K	HCO$_3$	Cl	SO$_4$	NO$_3$	pH	T, °C	SEC	Source	Aquifer
Unknown (4-9-16aab)	3/ 6/61	78	21	16*		309	19	32	2.2	7.8		600	KGS	C
Unknown (4-9-16bca)	5/14/49	75	14	24*		306	8.5	28	4.9	7.8			KGS	A
Unknown (2-3-35dc)	12/12/51	212	49	60*		425	13	467	7.5		13.0		KGS	B
Unknown (4-10-8cb)	12/14/51	92	20	103*		527	44	38	2.5		11.1		Walters (1954)	A
Unknown (4-10-11da)	12/13/50	85	15	37*		398	11	10	0.4				Walters (1954)	C
Unknown (5-9-22cc)	12/12/51	422	72	70*		412	37	1013	71		12.8		Walters (1954)	B
Unknown (5-9-24ba)	12/12/51	105	16	18*		399	8	23	6.2		12.2		Walters (1954)	B
Unknown (5-10-26dd)	12/12/51	78	24	63*		434	15	47	3.0				Walters (1954)	C

Notes: Concentrations expressed in mg/L.
SEC in micromhos/cm at 25°C.
A = alluvium; B = bedrock; C = glacial deposits; D = buried channel.
* Na plus K determined as the remainder from the charge balance equation.
KDHE = Kansas Department of Health and Environment; RWD3 = Rural Water District No. 3; KGS = Kansas Geological Survey.

HYDROGEOCHEMISTRY OF A BURIED PREGLACIAL CHANNEL
IN SOUTHEAST MARSHALL COUNTY, KANSAS

by

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The hydrogeology and ground-water geochemistry of a buried preglacial channel in southeast Marshall County, Kansas, have been investigated. Quaternary till and Permian limestones and shales comprise the surficial rocks of the area. Till thickness ranges up to 325 feet. The principal aquifer of the channel is a basal chert gravel that attains a maximum thickness of about 20 feet. Well yields up to 300 gpm are possible from the gravel.

The axis of the channel trends southeast, passing north of Frankfort and intersecting the Marshall-Nemaha County line near Vermillion. Available drill hole data indicate a gradient of about 4-5 feet per mile. The channel is broad and asymmetrical in cross section and is nearly 3 miles wide at the eastern county line. The Black Vermillion River southwest of Frankfort was probably part of this buried channel system during early Quaternary time. Recharge to the channel occurs where perennial streams intersect the buried channel. Robidoux Creek and Black Vermillion River a few miles north of Frankfort are the probable sources of most of the recharge to the buried channel. Bedrock, till, and channel gravels are defined as aquifers based on differences in rock type. There are substantial differences in water chemistry among these three aquifer types. Sixty-two ground-water samples were collected from 42 water wells in the area. The predominant water type in all aquifers is $Ca-HCO_3$, but $Ca-SO_4$-type waters occur in bedrock containing gypsum. The carbonate system provides the principal controls on the chemical evolution of ground waters in the area. Saturation indices and ratios of Ca/Mg indicate that calcite is a more important control than dolomite. Calcite saturation indices are lowest in channel ground waters and highest in bedrock aquifers; total dissolved solids concentrations are also lowest in channel ground waters.

The range and variation in total dissolved solids in channel waters are small; multiple samples collected from three of four channel wells varied only a few percent in dissolved solids during the period of sampling. Ground water from bedrock and to a lesser extent from till range and vary greatly in dissolved constituents. Variations appear to be related to changes in recharge diluting mineralized ground water. Nitrate concentrations are lowest in channel ground waters and highest in shallow, old wells, possibly indicating contaminants entered through a poor surface seal around the shallow wells. Sodium is probably released during solution of carbonates and evaporates and, along with K, is controlled by ion exchange on clays.